



J. Serb. Chem. Soc. 80 (6) 755–766 (2015)
JSCS–4755

Synthesis and spectroscopic characterization of mononuclear/binuclear organotin(IV) complexes with 1*H*-1,2,4-triazole-3-thiol: Comparative studies of their antibacterial/antifungal potencies

BUSHRA PARVEEN^{1*}, IFTIKHAR HUSSAIN BUKHARI¹, SAIRA SHAHZADI², SAQIB ALI², SHABBIR HUSSAIN¹, KULSOOM GHULAM ALI¹ and MUHAMMAD SHAHID³

¹Department of Chemistry, GC University, Faisalabad, Pakistan, ²Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan and ³Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad-38000, Pakistan

(Received 11 July 2014, revised 30 January, accepted 21 February 2015)

Abstract: A series of di- and tri-organotin(IV) complexes of the general formula, $R_2(\text{Cl})\text{SnL}$ (**1**: R = Me; **2**: R = Bu) and $R_3\text{SnL}$ (**3**: R = Bu; **4**: R = Ph) were synthesized by refluxing equivalent mole ratios of organotin(IV) chlorides ($R_2\text{SnCl}_2/R_3\text{SnCl}$) with 1*H*-1,2,4-triazole-3-thiol (LH) in dry methanol. The synthesized complexes (**1–4**) were further treated with CS_2 and $R_2\text{SnCl}_2/R_3\text{SnCl}$ in 1:1:1 mole ratio to yield homobimetallic complexes of the types $R_2(\text{Cl})\text{SnLCS}_2\text{Sn}(\text{Cl})R_2$ (**5**: R = Me; **6**: R = Bu) and $R_3\text{SnLCS}_2\text{SnR}_3$ (**7**: R = Bu; **8**: R = Ph). The ligand and the complexes were characterized by elemental microanalysis (CHNS), FT-IR and multinuclear NMR (¹H- and ¹³C-), and electron ionization mass spectrometry. The IR data demonstrated that the dithiocarbamate donor site of the ligand acts in a bidentate manner and that the geometry around Sn(IV) is trigonal bipyramidal in the solid state. The ¹H- and ¹³C-NMR data supported the tetrahedral geometry with thiol donor sites of the ligand while tetra- and penta-coordinated environments around dithiocarboxylate bound tin(IV) in the solution state. Mass spectrometric data supported well the structures of the synthesized complexes. The homobimetallic derivatives were found more active than the mononuclear organotin(IV) compounds and free ligand against various strains of bacteria and fungi.

Keywords: homobimetallic complex; organotin chloride; NMR; IR; mass spectra; antimicrobial study; 1*H*-1,2,4-triazole-3-thiol; dithiocarboxylate.

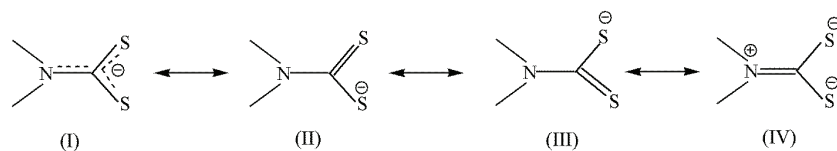
INTRODUCTION

Organotin(IV) compounds are amongst the most widely used organometallic compounds owing to the variety of their industrial and agricultural applications,

* Corresponding author. E-mail: bushra_nauman@hotmail.com
doi: 10.2298/JSC140711010P

including their use as pesticides, fungicides and anti-fouling agents.¹ Interest in the complexes of main group and transition metals with sulphur donor ligands is owed to their wide variety of structures and biological applications.^{2,3} Sulphur-containing organotin compounds are currently under investigations as chemoprotectants in platinum-based chemotherapy.⁴ In particular, thiocarbonyl and thiol donors have shown promising properties for chemical use in modulating cisplatin nephrotoxicity.⁵

Metal dithiocarboxylates are widely used in the vulcanization of rubber,⁶ as rodent repellents, as pesticides⁷ and as synthetic precursors for the formation of SnS nanocrystals by their solvothermal decomposition⁸ and are subjected to thermal and chemical vapour deposition (CVD) studies.⁹ The chemistry of organotin(IV) derivatives with sulphur ligands has grown with prolific speed on account of multifaceted reasons. One of the important structural consequences of dithiol ligands is the preferential stabilization of a specific stereochemistry in their metal complexes and they are considered as soft donors showing excellent coordination ability. Dithiocarbamate anions are highly effective ligands owing to the stability of the resulting metal dithiocarbamates, due to a significant contribution of the resonance forms, shown in Scheme 1 (structure IV), to the overall electronic structure.¹⁰



Scheme 1. Resonant forms of the $-\text{NCSS}^-$ moiety.

In view of structural importance and biological applications of organotins, a new series of di- and tri-alkyl/aryl tin derivatives of 1*H*-1,2,4-triazole-3-thiol ($\text{C}_2\text{H}_3\text{N}_3\text{S}$) were synthesized. The choice of the ligand was made based on that after insertion of CS_2 it has the simultaneous availability of thiol and dithiocarbamate donor sites, thus enabling its bimetallic complexation with organotin moieties. The products were characterized by elemental analysis, FT-IR, ^1H - and ^{13}C -NMR spectroscopy and mass spectrometry. These complexes were screened against various bacteria and fungi to investigate their possible use as antibacterial and antifungal agents.

EXPERIMENTAL

Chemicals and instrumentation

1*H*-1,2,4-Triazole-3-thiol, triphenyltin chloride, tributyltin chloride, dibutyltin dichloride and dimethyltin dichloride were purchased from Aldrich (USA) and were used without any further purification. CS_2 was obtained from Riedel-de-Haën. The organic solvents of analytical grade (chloroform, *n*-hexane, ethanol, methanol, DMSO and acetone) were procured

from Merck (UK). Nutrient agar, nutrient broth, and potato dextrose agar (PDA) were purchased from Oxoid Company (UK). The solvents were dried by standard procedures.¹¹ Melting points were determined in capillary tubes on an electrothermal melting point apparatus, model Stuart SMP3 (UK), and are uncorrected. The percentage composition of carbon, hydrogen, nitrogen and sulphur were determined using a CHNS-932 Leco (USA). The FT-IR spectra in the range of 4000–250 cm^{-1} were obtained on a Thermo Nicolet-6700 FT-IR spectrophotometer. The NMR spectra were recorded on a Bruker AM-250MHz FT-NMR spectrometer (Germany). Mass spectral data were measured on a JEOL JMS 600-H mass spectrometry in the ionization mode at 70 eV. The antimicrobial activities were determined in an incubator (Sanyo, Germany) and sterilized in an autoclave (Omron, Japan).

Physical, analytical and spectral data of the synthesized compounds are given in Supplementary material to this paper.

General procedure for the synthesis of the homobimetallic complexes

Step-1. 1H-1,2,4-Triazole-3-thiol (1 mmol) and $\text{R}_2\text{SnCl}_2/\text{R}_3\text{SnCl}$ (1 mmol) were refluxed together in 20 mL dry methanol for 6 h.¹² The solvent was evaporated under reduced pressure on a rotary evaporator. The formed precipitates were filtered and dried in open air. The product was recrystallized from ethanol.

Step-2. The product (1 mmol) obtained in 1st step was dissolved in methanol (15 mL) in a round-bottom two-necked flask with stirring. To the above solution, CS_2 (1 mmol) was added dropwise at room temperature and the reaction mixture was stirred for 30 min.¹³ Then $\text{R}_2\text{SnCl}_2/\text{R}_3\text{SnCl}$ was added in 1:1 mole ratio and the reaction mixture was refluxed for 6–7 h (Scheme 2). The solvent was evaporated slowly at room temperature and the product was dried in air. The product was recrystallized from ethanol.

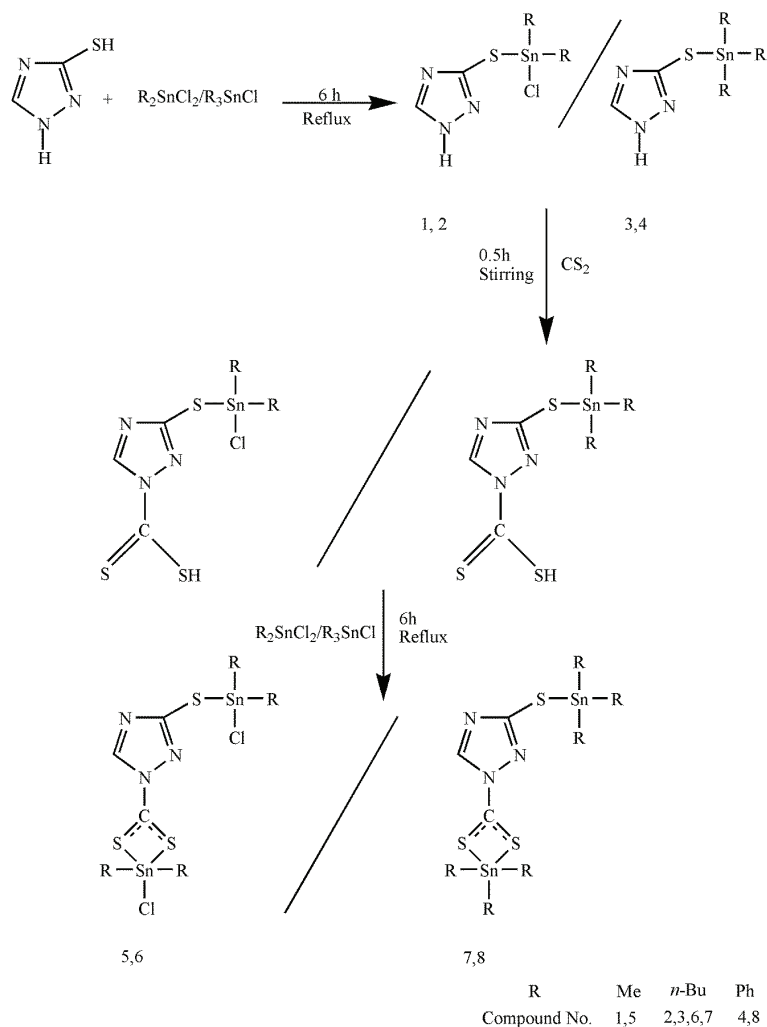
Antimicrobial activities

Growth medium, culture and inoculum preparation. The bacterial strains (*Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus* and *Pasteurella multocida*) were cultured in nutrient agar medium at 37 °C overnight. The pure bacterial cultures obtained were maintained in the medium in slants and Petri plates. For inoculums preparation, 13 g of nutrient broth was added to one litre of distilled water, mixed homogenously and was autoclaved for 15 min at 121 °C. Then 10 μL of pure culture of a bacterial strain was added to this freshly prepared nutrient broth medium (100 mL) and incubated in a shaker (140 rpm) at 37 °C for 24 h. The prepared inocula were stored at 4 °C. Inocula with 1×10^8 spores mL^{-1} were used for further analysis.

The fungal strains (*Aspergillus niger*, *Aspergillus flavus*, *Rhizoctonia solani* and *Alternaria alternata*) were cultured in potato dextrose agar medium overnight at 28 °C. The pure cultures were maintained in Sabouraud dextrose agar (SDA) medium in slants and Petri plates, which had been pre-sterilized in a hot air oven at 180 °C for 3 h. These cultured slants were incubated at 28 °C for multiplication of fungal strains for 3–4 days.

Antibacterial/antifungal assay by the disc diffusion method. The antibacterial and antifungal activities of the ligand and the synthesized complexes were determined by the disc diffusion method.¹⁴ For medium preparation, 2.8 g of nutrient agar (for the antibacterial activities) or 3.9 g of potato dextrose agar (for the antifungal activities) was suspended in 100 mL distilled water and mixed well to distribute homogenously. After this, the medium was sterilized by autoclaving at 121 °C for 15 min, mixed well with 100 μL inoculums and transferred into the sterilized Petri plates. Then small filter paper discs (size, 9 mm) each soaked with 100 μL solution of a test sample were placed flat on the growth medium and the

Petri plates were incubated for 24 h at 37 °C for the bacterial growth and for 48 h at 28 °C for the fungal growth. The biologically active samples inhibited the bacterial/fungal growth to form clear zones. A zone reader was used to measure the zones of inhibition in mm.



Scheme 2. Synthesis of the homobimetallic complexes.

Statistical analysis

The antimicrobial activity data are presented in the tabulation mode along with their mean, standard deviation and the data were tested by one-way ANOVA.¹⁵

RESULTS AND DISCUSSION

The synthesized complexes were solid and stable in air. They had sharp melting points and were soluble in common organic solvents. The elemental (C,

H, N and S) analysis data agreed very well with the proposed formulas of the complexes. The physical data of ligand and its complexes are summarized in Table S-I of the Supplementary material to this paper.

Infrared spectroscopy

IR spectra of HL and complexes were recorded in the range of 4000 to 250 cm^{-1} and data is given in Table S-II of the Supplementary material. The values related to different functional groups were assigned by comparison of the spectra of the complexes with that of the free ligand. The precursor ligand (LH) exhibited a broad band at 2560 cm^{-1} due to $\nu(\text{S-H})$ vibrations. This band was absent in the spectra of complexes **1-8** due to sulphur-tin coordination, which was also confirmed by the appearance of $\nu(\text{Sn-S})$ bands in the region 437–471 cm^{-1} in the spectra of the complexes.¹⁶ All the complexes displayed a sharp Sn-C peak in the range 535–563 cm^{-1} , except for triphenyltin(IV) derivatives, for which a weak vibration appeared at 263–265 cm^{-1} due to Sn-C stretching.¹⁷ The chlor-diorganotin derivatives **1, 2, 5** and **6** displayed a peak associated with $\nu(\text{Sn-Cl})$ in the region 320–336 cm^{-1} .¹⁸

In the free ligand, $\nu(\text{NH})$ band appeared at 3148 cm^{-1} ; the maintenance of this band in almost the same region (3143–3149 cm^{-1}) in complexes **1-4** evidently described the non-involvement of the imino nitrogen in bonding with tin. However, the $\nu(\text{NH})$ stretching vibration was absent in the spectra of complexes **5-8** due to insertion of CS_2 and the consequent bonding of the dithiocarbamate moiety with tin. Thus, new bands appeared for $\nu(\text{C-S})$ and $\nu(\text{C-N})$ stretching vibrations that gave valuable information about the coordination behaviour of the dithiocarbamate group (N-CSS) to the tin atom. In the IR spectra of complexes **5-8**, the strong peaks at 1034–1051 cm^{-1} and 963–976 cm^{-1} were assigned to the asymmetric absorption $\nu(\text{CS}_2)_{\text{asym}}$ and the symmetric absorption $\nu(\text{CS}_2)_{\text{sym}}$ frequencies, respectively. According to the literature,¹⁹ the differences between $\nu(\text{CS}_2)_{\text{asym}}$ and $\nu(\text{CS}_2)_{\text{sym}}$ of 68–79 cm^{-1} for complexes **5-8** indicated that the 1,1-dithioate moiety was linked to the central tin in a bidentate fashion. The values of $\nu(\text{N-CSS})$ stretching vibrations (1456–1505 cm^{-1}) fall between those reported for C-N single bond (1250–1360 cm^{-1}) and C=N double bond (1640–1690 cm^{-1}), which is an indication of the partial double bond character of the C-N bond.^{16,20} A partial double bond character for the C-N bond would result in some partial double bond character for the C-S bonds, as a result both the sulphur atoms were involved in coordination with the metal, resulting in bidentate coordination¹⁶ and pentacoordinated geometry.²¹ This interaction could be viewed as the coordination of one normal Sn-S bond and one weak Sn-S bond. A weak Sn-S bond is possibly through π overlap of the empty d-orbitals of the tin atom and the p-orbitals of sulphur.

¹H-NMR

The ¹H-NMR spectra were recorded for compounds **1–8** in DMSO-*d*₆. The characteristic chemical shifts (Table S-III of the Supplementary material) were recognized by their intensity and multiplicity patterns. The numbers of protons, calculated from the integration curves, were in agreement with the proposed molecular structure theoretically calculated by the incremental method.²² The singlet resonance at 13.357 ppm for –SH proton of the free ligand (HL) was absent in the spectra of all the complexes **1–8** and was taken as verification of thiol–tin coordination.²³ The signal at 11.48 ppm for the imino proton of the free ligand persisted in the spectra of complexes **1–4**, indicating its non-involvement in coordination; however, this signal was absent in the spectra of complexes **5–8**, due to insertion of –CSS in order to develop the dithiocarbamate–tin linkage. New signals in the expected range for the organotin moieties were evidence for complex formation.^{23,24} In the *n*-butyl derivatives **2**, **3**, **6** and **7**, the terminal methyl protons absorb at 0.87–0.80 ppm as a triplet with a ³*J*(¹H–¹H) coupling constant of 7.0–7.2 Hz, while the α-CH₂, β-CH₂ and γ-CH₂ protons appear as multiplets.²⁵ In the dimethyltin(IV) derivative **5**, the CH₃ protons gave a sharp singlet at 1.46 ppm^{23,26} with a ²*J*[¹¹⁹Sn–¹H] coupling constant of 79 Hz, which corresponds to trigonal bipyramidal geometry of tin in the solution state. In the triphenyltin derivatives **4** and **8**, the phenyl group attached to the Sn atom gave complex multiplets in the range of 7.31–7.96 ppm.²⁷

¹³C-NMR

The characteristic resonance signals in the ¹³C-NMR spectra of the selected complexes, recorded in DMSO, are given in Table S-IV of the Supplementary material. The upfield resonance shift of the SH bonded carbon (labelled as 2) from 165.57 ppm in the free ligand to 152.11–154.33 ppm in the complexes, indicates that the ligand acts in the thiolate form and this carbon is deshielded upon complexation of the ligand to the positive Sn center.²³ The –CSS group in the complexes gave a signal in the range 191.36–194.85 ppm, indicating the coordination of sulphur to tin. The methyl group linked to the Sn atom in complex **5** gave a sharp signal at 10.6 ppm.²⁸ Complexes **6** and **7** showed signals of the *n*-butyl group in the range of 13.5–14.7 ppm (for CH₃) and 25.4–29.3 ppm (for CH₂).²⁹ In complex **8**, the phenyl carbons gave signals in the range 129.5–138.1 ppm in the ¹³C-NMR spectra, as reported earlier.³⁰

In order to gain further information regarding the possible coordination geometries in solution, the ¹*J*[¹¹⁹Sn–¹³C] and ²*J*[¹¹⁹Sn–¹H] coupling constants were examined closely, as structural details, such as the determination of C–Sn–C bond angles, can be obtained by use of the methods reported in the literature.^{31,32} The C–Sn–C bond angles, calculated by application of the Lockhart equation^{31,32} are given in Table S-V of the Supplementary material; the data strongly supports

the trigonal bipyramidal geometries in the chlorodialkyltin(IV) derivatives **5** and **6**, while a tetrahedrally coordinated metal centre was supported in the tributyltin(IV) complex **7**.

Mass spectrometry

The conventional EI mass spectral data at 70 eV for both the ligand and the complexes were recorded along with m/z and intensity, which are listed in Table S-VI of the Supplementary material. In mass spectral data of the compounds, each fragment ion occurred in a group of peaks as a result of tin isotopes. For simplicity, the mass spectral fragmentation data reported here are related to the principal isotope ^{120}Sn or $^{120}\text{Sn}^{35}\text{Cl}$ peak in each species, and must be regarded as approximate.³³ The molecular ion peaks, M^+ , are either not observed or if observed have very low intensities in synthesized organotin complexes. The fragmented ions are in good agreement with the expected structure of the compounds and consistent with the literature.^{34,35} For the triorganotin compounds, the primary fragmentation from the molecular ion appeared in two ways. The first one was initiated with the loss of R (R = Bu or Ph), whereas the second fragmentation was due to the loss of ligand (L). For complexes **3** and **4**, the former pattern predominated and gave $\text{C}_2\text{H}_2\text{N}_3\text{SSnR}_2^+$ species, which could then lose either R–R or R in two successive steps to form further EE^+ . The $[\text{R}_3\text{Sn}]^+$, formed by the loss of the ligand part, forms a $[\text{Sn}]^+$ fragment by the successive elimination of the R radical. Somewhat different mass fragments were suggested for the diorganotin compounds, but these pathways end up in a similar fashion as suggested for the triorganotin compounds. In addition, the following ions were also observed with reasonable intensities in the mass spectra of all organotin(IV) derivatives, $[\text{C}_6\text{H}_5]^+$, $[\text{C}_4\text{H}_9]^+$ and $[\text{CH}_3]^+$.

Antibacterial activity

The synthesized complexes and free ligand were screened for their *in vitro* antibacterial activities by the disc diffusion method¹¹ against *S. aureus*, *E. coli*, *B. subtilis* and *P. multocida*, and the results were summarized in Table I. The data revealed that the synthesized complexes had significant antimicrobial activities against the pathogenic bacteria as compared to the ligand, which indicates that metallation increased antibacterial activity in accordance with earlier reports.³⁶ This higher activity may be ascribed to the Tweedy theory, according to which chelation reduces the polarity of the central metal atom because of partial sharing of its positive charge with the ligand, which favours the permeation of the complex through the lipid layer of the membrane.^{37,38}

In general, the triorganotin(IV) complexes were found to be more active than the diorganotin(IV) complexes, a trend consistent with an earlier report.³⁹ Complex **8** showed strong antibacterial activity against *E. coli*, while complexes **1** and **5** exhibited strong antibacterial activity against *P. multocida*.

TABLE I. Antibacterial activity (bacterial inhibition zone, mm) data of organotin(IV) complexes **1–8**; concentration = 10 mg mL⁻¹ in DMSO; standard = rifampicin. The antibacterial values are mean±SD of three samples analyzed individually in triplicate. Different letters in superscripts indicate significant differences; a = maximum activity, b = intermediate activity, c = minimum activity, ab = activity between maximum and intermediate and bc = activity between intermediate and minimum

Compd.	Bacterium			
	<i>S. aureus</i>	<i>E. coli</i>	<i>B. subtilis</i>	<i>P. multocida</i>
HL	11.2 ^c ±0.7	16.1 ^c ±0.1	12.2 ^c ±0.7	13.2 ^c ±0.7
1	17 ^b ±0.5	24.5 ^b ±0.5	19.5 ^{bc} ±0.1	22.5 ^{ab} ±1.0
2	14.5 ^{bc} ±0.7	19 ^{bc} ±0.5	14 ^{bc} ±0.2	15.1 ^{bc} ±0.1
3	16 ^b ±0.5	25.2 ^{ab} ±0.7	15.5 ^{bc} ±0.1	14.5 ^{bc} ±0.1
4	19.5 ^{ab} ±0.1	27.8 ^{ab} ±0.7	21 ^{ab} ±0.1	20.2 ^{ab} ±0.5
5	16 ^b ±0.5	26.5 ^{ab} ±0.5	21.5 ^b ±0.5	23.8 ^{ab} ±0.1
6	17 ^b ±0.5	21.8 ^{bc} ±0.1	15.5 ^{bc} ±0.5	16.3 ^{bc} ±0.5
7	17.5 ^b ±0.1	26 ^{ab} ±0.5	17 ^{ab} ±0.5	19 ^b ±0.5
8	22 ^{ab} ±0.5	28.3 ^{ab} ±0.1	22.3 ^{ab} ±0.7	15.5 ^{bc} ±0.1
Standard	32 ^a ±0.5	38 ^a ±0.7	30 ^a ±0.5	37 ^a ±0.5

The variation in the trends for these compounds may be explained based on three possible factors, *i.e.*, lipophilic character, diffusion and on the bacterial strain. The former two factors are associated with complexes. The lipophilic character increased with increasing chain length whereas diffusion has an inverse effect. The enhanced activities of the triorganotin complexes could be well described by the lipophilic character. In some cases, the diorganotin complexes were found more active, *e.g.*, in dimethyltin complexes due to dominating diffusive nature of small methyl group. The reported bimetallic organotin(IV) complexes show enhanced antibacterial activity compared to monometallic organotin(IV) complexes.^{40,41} No compound showed better inhibitory action than the standard drug.

Antifungal activity

The disc diffusion method was employed to test the antifungal activities of the synthesized compounds against four different strains of fungi, *A. niger*, *A. flavus*, *R. solani* and *A. alternata* and fluconazole was used as the standard drug. The results are shown in Table II. The complexes exhibited greater antifungal potentials than the precursor ligand, which may be due to the chelation and the presence of sulphur atoms.⁴² The triorganotin(IV) derivatives were more active than the diorganotin(IV) complexes against the fungal strains and even more than the standard drug. The higher activity of complex **3** may be due to highest lipophilic character of the tributyltin(IV) derivatives.⁴³ That the homobimetallic complexes showed greater activity might be due to the presence of two Sn atoms.^{13,40,41}

TABLE II. Antifungal activity data (fungal inhibition zone, mm) of organotin(IV) complexes **1–8**; concentration = 10 mg/mL in DMSO; standard = fluconazole. The antifungal values are mean±SD of three samples analyzed individually in triplicate. Different letters in superscripts indicate significant differences; a = maximum activity, b = intermediate activity, c = minimum activity, ab = activity between maximum and intermediate and bc = activity between intermediate and minimum

Compd.	Fungus			
	<i>A. niger</i>	<i>A. flavus</i>	<i>R. solani</i>	<i>A. alternata</i>
HL	10.2 ^c ±0.5	13.2 ^c ±0.8	8.0 ^c ±1.0	10.0 ^c ±0.5
1	11.2 ^c ±0.3	13.9 ^c ±0.5	10.2 ^c ±0.1	19.2 ^{bc} ±1.0
2	21.6 ^{bc} ±0.7	10.1 ^c ±0.4	9.0 ^c ±0.2	23.2 ^{bc} ±0.1
3	44 ^{ab} ±0.5	46.4 ^a ±0.2	36 ^{ab} ±0.5	36.0 ^{ab} ±0.5
4	36 ^{ab} ±1.2	32.3 ^{ab} ±0.2	31.2 ^{bc} ±0.3	35.2 ^{bc} ±1.0
5	11.5 ^c ±0.3	13.5 ^c ±0.5	10.1 ^c ±0.5	22.3 ^{bc} ±0.1
6	21.5 ^{bc} ±0.7	10.5 ^c ±0.7	8.6 ^c ±0.5	21.3 ^{bc} ±0.5
7	49.2 ^a ±0.5	48.2 ^a ±0.1	54 ^a ±0.7	42.8 ^a ±0.1
8	39 ^{ab} ±0.5	41.5 ^a ±0.5	34.3 ^{ab} ±0.1	38.8 ^{ab} ±0.5
Standard	26 ^b ±0.5	28 ^b ±0.5	30 ^b ±0.5	29.2 ^b ±0.5

CONCLUSIONS

Homobimetallic complexes of organotin(IV) with a sulphur–sulphur donor ligand (1*H*-1,2,4-triazole-3-thiol) were synthesized under reflux. An IR study confirms the dithiocarbamate donor site of the ligand acts in a bidentate manner and showed trigonal bipyramidal geometry around Sn(IV) in the solid state. NMR data revealed that the tetrahedral geometry with thiol donor sites of the ligand while tetra- and penta-coordinated environments around dithiocarbamate bound tin(IV) in the solution state. Mass spectrometric and elemental analysis data supported the solid and solution spectroscopic results. Antimicrobial results revealed that the activity was enhanced upon coordination with tin. In addition, the triorganotin(IV) derivatives superseded the diorganotin(IV) compounds in their antimicrobial action. Such a study would be helpful in the design of novel metal-based drugs.

SUPPLEMENTARY MATERIAL

The physical, analytical and spectral data of the synthesized complexes, Tables S-I–S-VI, are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

Acknowledgment. Bushra Parveen thanks the Higher Education Commission, Islamabad, Pakistan, for financial support under the PhD Fellowship Scheme Batch-VI (PIN Code: 106-2038-ps6-083).

ИЗВОД

СИНТЕЗА И СПЕКТРОСКОПСКА КАРАКТЕРИЗАЦИЈА МОНО- И ДИНУКЛЕАРНИХ КОМПЛЕКСА КАЛАЈА(IV) СА 1H-1,2,4-ТРИАЗОЛ-3-ТИОЛОМ: УПОРЕДНА ИЗУЧАВАЊА ЊИХОВЕ АНТИБАКТЕРИЈСКЕ И АНТИФУНГАЛНЕ АКТИВНОСТИ

BUSHRA PARVEEN¹, IFTIKHAR HUSSAIN BUKHARI¹, SAIRA SHAHZADI², SAQIB ALI², SHABBIR HUSSAIN¹, KULSOOM GHULAM ALI¹ и MUHAMMAD SHAHID³¹Department of Chemistry, GC University, Faisalabad, Pakistan, ²Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan and ³Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad-38000, Pakistan

Синтетисана је серија ди- и триоргано комплекса калаја(IV), опште формуле $R_2(Cl)SnL$ (**1**: R = Me; **2**: R = Bu) и R_3SnL (**3**: R = Bu; **4**: R = Ph). Комплекси су синтетисани рефлуксом еквимоларних количина калај(IV)-хлорида (R_2SnCl_2/R_3SnCl) и 1H-1,2,4-триазол-3-тиола (LH) у сувом метанолу као растварачу. Овако синтетисани комплекси **1–4** су након третирања са CS_2 и R_2SnCl_2/R_3SnCl (у молском односу 1:1:1) наградили полинуклеарне Sn(IV) комплексе, опште формуле $R_2(Cl)SnLCS_2Sn(Cl)R_2$ (**5**: R = Me; **6**: R = Bu) and $R_3SnLCS_2SnR_3$ (**7**: R = Bu; **8**: R = Ph). Полазни лиганд и комплекси су окарактерисани помоћу елементалне микроанализе, FT-IR и NMR (¹H- и ¹³C-) спектроскопије, као и масене спектрометрије. На основу IR података закључено је да се испитивани лиганд преко дитиокарбаматног дела молекула бидентатно координује формирајући у чврстом стању тригонално-бипиримидалну геометрију Sn(IV) комплекса. На основу ¹H- и ¹³C-NMR испитивања у раствору нађено је да се испитивани лиганд координује преко тиолног атома сумпора и гради тетраедарску геометрију комплекса, док се у случају дитиокарбоксилатне координације лиганда граде комплекси са тетра- и пентакоординационом сфером око калаја(IV). Резултати добијени на основу масене спектрометрије су у сагласности са спектроскопски претпостављеном геометријом испитиваних комплекса. На основу испитивања активности на различитим сојевима бактерија и гљива закључено је да су полинуклеарни комплекси активнији од одговарајућих мононуклеарних Sn(IV) комплекса.

(Примљено 11. јула 2014, ревидирано 30. јануара, прихваћено 21. фебруара 2015)

REFERENCES

1. M. Gielen, A. G. Davies, K. Pannell, E. Tiekink, Eds., *Tin Chemistry: Fundamentals, Frontiers and Applications*, Wiley, Chichester, 2008
2. S. Shahzadi, S. Ali, *J. Iran. Chem. Soc.* **5** (2008) 16
3. E. R. T. Tiekink, *Appl. Organomet. Chem.* **22** (2008) 533
4. N. Ferrell, *Transition in Catalysis by Metal Complexes*, Vol. 11, B. R. James, R. Ugo, Eds., Kluwer, Dordrecht, 1989, p. 44
5. R. T. Dorr, H. M. Pinedo, J. H. Schornagel, *Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy*, Vol. 2, Plenum Press, New York, 1996, p. 131
6. P. J. Nieuwenhuizen, J. Reedijk, M. Van Duin, W. J. McGill, *Rubber Chem. Technol.* **70** (1997) 368
7. M. Cicotti, *Handbook of Residue Analytical Methods for Agrochemicals*, Vol. 2, Wiley, Chichester, 2003
8. D. C. Menezes, G. M. De Lima, A. O. Porto, C. L. Donnici, J. D. Ardisson, A. C. Doriguetto, J. Ellena, *Polyhedron* **23** (2004) 2103
9. A. T. Kana, T. G. Hibbert, M. F. Mahon, K. C. Molloy, I. P. Parkin, L. S. Price, *Polyhedron* **20** (2001) 2989

10. Zia-ur-Rehman, N. Muhammada, S. Shuja, S. Ali, I. S. Butler, A. Meetsma, M. Khan, *Polyhedron* **28** (2009) 3439
11. W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, Elsevier, New York, 2003
12. T. R. Fritsche, M. Dermott, T. R. Shryock, R. D. Walker, *J. Clin. Microbiol.* **45** (2007) 2758
13. J. Anwer, S. Ali, S. Shahzadi, M. Shahid, S. K. Sharma, K. Qanungo, *J. Coord. Chem.* **66** (2013) 1142
14. Zia-ur-Rehman, M. M. Barsan, I. Wharf, N. Muhammad, S. Ali, A. Meetsma, I. S. Butler, *Inorg. Chim. Acta* **361** (2008) 3322
15. F. G. D. Steel, J. H. Torrie, D. A. Dikey, *Principles and Procedures of Statistics: a Biometrical Approach*, 3rd ed., McGraw Hill, New York, 1997
16. S. Hussain, S. Ali, S. Shahzadi, S. K. Sharma, K. Qanungo, M. Altaf, H. S. Evans, *Phosphorus Sulfur Silicon Relat. Elem.* **186** (2011) 542
17. M. Rizwan, S. Ali, S. Shahzadi, S. K. Sharma, K. Qanungo, M. Shahid, S. Mahmood, *J. Coord. Chem.* **67** (2014) 341
18. A. A. Soliman, G. G. Mohammed, *Thermochim. Acta* **42** (2004) 151
19. I. Baba, A. F. Abdul-Muthalib, Y. F. Abdul-Aziz, N. S. Weng, *Phosphorus Sulfur Silicon Relat. Elem.* **186** (2011) 1326
20. S. Thirumaran, K. Ramalingam, *Transition Met. Chem.* **25** (2000) 60
21. H. L. Singh, A. K. Varshney, *Appl. Organomet. Chem.* **15** (2001) 762
22. H. O. Kalinowski, S. Berger, S. Braun, *¹³C NMR Spektroskopie*, Vol. 56, Thieme, Stuttgart, 1984, p. 133
23. C. Ma, J. Li, R. Zhang, *Heteroatom Chem.* **17** (2006) 353
24. R. Singh, N. K. Kaushik, *Spectrochim. Acta, A* **72** (2009) 691
25. M. Nath, M. Sulaxna, X. Song, G. Eng, *J. Organomet. Chem.* **691** (2006) 1649
26. Q. Wang, Q. C. Ma, G. He, Y. Li, *Heteroatom Chem.* **23**(2012) 531
27. M. Hussain, M. Zaman, M. Hanif, S. Ali, M. Danish, *J. Serb. Chem. Soc.* **73** (2008) 179
28. M. Careri, A. Mangla, G. Predieri, C. Vignali, *J. Organomet. Chem.* **375** (1989) 39
29. S. Shahzadi, S. Ali, M. H. Bhatti, M. Fettouhi, M. Athar, *J. Organomet. Chem.* **691** (2006) 1797
30. Y. F. Win, S. G. Teoh, T. S. T. Muhammad, Y. Sivasothy, S. T. Ha, *Am. J. Appl. Sci.* **301** (2010) 31
31. T. P. Lockhart, W. F. Manders, *Inorg. Chem.* **25** (1986) 892
32. J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, *J. Organomet. Chem.* **315** (1986) 299
33. A. G. Davies, *Organotin Chemistry*, 2nd ed., Wiley-VCH, Weinheim, 2004, pp. 17–22
34. Zia-ur-Rehman, N. Muhammad, S. Ali, I. S. Butler, A. Meetsma, *Inorg. Chim. Acta* **373** (2011) 187
35. A. Tarassoli, T. Sedaghat, B. Neumuller, M. Ghassemzadeh, *Inorg. Chim. Acta* **318** (2001) 15
36. E. R. T. Tiekink, *Appl. Organomet. Chem.* **22** (2008) 533
37. B. G. Tweedy, *Phytopathology* **55** (1964) 910
38. S. S. Konstantinović, B. C. Radovanović, S. P. Sovilj, S. Stanojević, *J. Serb. Chem. Soc.* **73** (2008) 7
39. K. Tahira, S. Ali, S. Shahzadi, S. K. Sharma, K. Qanungo, *J. Coord. Chem.* **64** (2011) 1871
40. M. K. Samota, G. Seth, *Heteroatom Chem.* **21** (2010) 44
41. L. Dostal, R. Jambor, A. Ruzicka, R. Jirasko, J. Taraba, J. Holecek, *J. Organomet. Chem.* **692** (2007) 3750

42. T. R. Fritsche, P. F. McDermott, T. R. Shryock, R. D. Walker, *J. Clin. Microbiol.* **45** (2007) 2758
43. G. J. M. van der Kerk, J. G. A. Luijten, *J. Appl. Chem.* **6** (1956) 56.