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Synthesis, Characterization and Antibacterial Screening Activity of Dibutyltin(IV) and Triphenyltin(IV) Complexes Derivatives of 2,4-Dinitrobenzoic and 3,5-Dinitrobenzoic Acids

YIP-FOO WIN[1,2,*], SIANG-GUAN TEOH[2,*] and EMAD YOUSIF[3]

[1]Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Perak Campus, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
[2]School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden Penang, Pulau Pinang, Malaysia
[3]Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

*Corresponding authors: Fax +605 4661676; Tel: +605 4688888; E-mail: williamyfw@yahoo.com

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In this work, five organotin(IV) carboxylate derivatives of 2,4-dinitrobenzoic and 3,5-dinitrobenzoic acids have been successfully synthesized and characterized quantitatively and qualitatively. Results of the spectroscopy studies indicated that the coordination took place *via* oxygen atoms from the carboxylate anions to the tin atom moieties. From the NMR study, toluene molecule was presented in complexes **3** and **4** which have been clarified and identified. From the preliminary *in vitro* antibacterial screening study, all the complexes showed some moderate and selective activity against the tested bacterial strains.

Key Words: 2,4-Dinitrobenzoic acid, 3,5-Dinitrobenzoic acid, Antibacterial activity, Organotin(IV) carboxylate.

INTRODUCTION

Nowadays, the synthesis, characterization and structural study of organotin(IV) complexes have been well-known, established and documented since the first organotin(IV) compound was successfully isolated in 1850s[1-7]. The interest and application of organotin(IV) carboxylate complexes have also received considerable attention as these complexes display a large array of applications in industries as catalysts, antifouling agents, wood preservatives, crop protection agents, *etc.*[1]. Up-to-date, organotin(IV) carboxylate complexes are extensively studied due to the structural diversity (monomer, dimeric, hexameric and oligomeric) and its biological properties[1-15].

As part of our interest and research on organotin(IV) work, we have synthesized and characterized organotin(IV) carboxylate complexes derivatives of 2,4-dinitrobenzoic acid, 2,4-$(NO_2)_2C_6H_3COOH$ and 3,5-dinitrobenzoic acid, 3,4-$(NO_2)_2C_6H_3COOH$. In addition, the preliminary *in vitro* antibacterial screening activity of the complexes obtained are carried out and the results are reported herein.

EXPERIMENTAL

All the reagents and solvents were purchased commercially and used without any further purification. Infrared spectra were recorded using a Perkin-Elmer FTIR GX Spectrophotometer as KBr disc in the frequency range of 4000-400 cm^{-1}. The ^1H, ^1H-^{13}C HMQC and ^{119}Sn NMR were recorded on a Bruker AC-P 400MHz FTNMR Spectrometer and ^{13}C NMR was recorded on a Bruker AC-P 300MHz FTNMR Spectrometer using deuterated $CDCl_3$ and DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard. Elemental C, H and N analyses were carried out on a Fison EA 1108 CHNS-O analyzer. Tin was determined gravimetrically by igniting a known quantity of each complex to SnO_2. The melting points were determined in an open capillary and were uncorrected.

Preliminary *in vitro* antibacterial screening activity: The synthesized complexes and acids were screened for their *in vitro* antibacterial activity against three gram-negative (*Escherichia coli*, *Pseudomonas aeruginosa* and *Klebsiella pneumoniae*) and two gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) bacterial strains, by inhibition zone method using agar well diffusion method. The seeded agar (nutrient agar medium) was prepared by cooling the molten agar to 40 ºC and then adding bacterial inoculums containing approximately 10^4-10^6 colony forming units (CFU)/mL. The bacterial inoculums were spread on the plate containing agar medium and even coverage was ensured before the agar solidified. The complexes were dissolved in DMSO to prepare 1.0 mg/mL concentration. By using a sterile metallic borer, the wells (6 mm in diameter) were dug and the standard drugs

and complexes were introduced into the respective wells. The plates were incubated immediately at 37 ºC for 20-24 h. The activity was determined by measuring the diameter of the inhibition zone (in mm).

Preparation of sodium salts and complexes: The sodium salts of the respective acids were obtained by heating under reflux a 1:1 molar ratio mixture of sodium hydroxide, NaOH (3 mmol) with the respective acids (3 mmol) in ethanol (50 mL) for 2 h. After a few days, white precipitate was obtained. Complexes **1**-**5** were synthesized by heating under reflux an equivalent molar ratio mixture of parent organotin(IV) [dibutyltin(IV) oxide or triphenyltin(IV) hydroxide] with the respective acids in appropriate solvents (50-60 mL) for few hours. Then, the respective clear yellow transparent solutions were isolated by filtration and kept in a bottle. After few days, yellow crystals were collected and washed with a small quantity of polar solvent.

RESULTS AND DISCUSSION

Complexes **1-5** have been obtained in solid state and gave a sharp melting point indicating that the isolation of fairly pure complexes and the micro-elemental analysis for C, H, N and Sn data obtained were in agreement with the predicted formula. The micro-elemental and melting point of complexes **1**-**5** are given in Table-1 and an outline of the proposed reactions and structure for complexes **1-5** are depicted in Fig. 1. For better clarity, all the crystal structure data of complexes **1-5** (except complex **4**) have been reported by our research group[9-12].

The characteristic infrared absorption frequencies (cm^{-1}) and assignments for important absorption bands of the acids, sodium salts and complexes **1-5** are listed in Table-2. The infrared spectra of complexes **1-5** revealed the distinct differences from those of their respective acids. The ν(O-H) bands which appeared in the range of 2884-2465 cm^{-1} for the respective acids were absent from the infrared spectra of the sodium salts and complexes **1-5**. In addition, infrared spectra of complexes **1-5** also revealed that the $\nu(COO)_{as}$ was shifted to a lower wavelength number compared to the parent acids. These two distinct appearances indicating the deprotonation and coordination of the carboxylate anions to the tin atom moieties as discussed and reported[7].

The ^{1}H NMR spectral data of complexes **1-5** are summarized in Table-3, the ^{1}H NMR spectra of complex **3** is depicted in Fig. 2 as a representative; the ^{13}C and ^{119}Sn NMR spectral data of complexes **1-5** are given in Table-4. In general, all the aliphatic groups are located in the upfield regions whereas the aromatic groups could be found in the downfield regions in the NMR spectra. Based on the ^{1}H and ^{13}C NMR study, the only exceptional case was the occurrence of toluene molecule in complexes **3** and **4** which have been clarified and identified in our previous report[7]. From the ^{119}Sn NMR study, the tin atom in complex **3** was five-coordinated as the chemical shifts $\delta(^{119}Sn)$ = -127.78 ppm fall in the range between -90 to -190 ppm which was assigned for five-coordinated tin atom[16]. Complexes **1** and **4** were organodistannoxane dimer types and exhibited two well resolved $\delta(^{119}Sn)$ signals as usually expected (**1** = -190.69, -193.80 ppm and complex **4** = -194.27, -203.44 ppm)[16]. From the ^{119}Sn NMR study, all the tin atoms in complexes **1**, **3** and **4** were five-coordinated and exhibited distorted trigonal bipyramid geometry. The chemical shifts $\delta(^{119}Sn)$ of triphenyltin(IV) carboxylate complexes showed a distinct different from the diorganotin(IV) carboxylate complexes[17,18]. Holecek *et al.*[17,18] has proposed that for four-coordinated triphenyltin(IV) carboxylate complexes, the chemical shifts $\delta(^{119}Sn)$ lie between -40 to -120 ppm. In this study, complexes

TABLE-1
MELTING POINT AND MICRO-ELEMENTAL ANALYSIS DATA OF COMPLEXES **1-5**

Complexes	Yield (%)	m.p. (ºC)	Elemental (%)			
			C	H	N	Sn
$[\{2,4\text{-}(NO_2)_2C_6H_3COO(C_4H_9)_2Sn\}_2O]$ **1**	87.2	197.8-198.6	40.11 (39.86)	4.86 (4.68)	6.23 (6.20)	26.12 (26.26)
$2,4\text{-}(NO_2)_2C_6H_3COO(C_6H_5)_3Sn$ **2**	82.3	160.4-161.2	53.31 (53.51)	3.00 (3.23)	4.91 (5.00)	21.03 (21.15)
$\{3,5\text{-}(NO_2)_2C_6H_3COO\}_2(C_4H_9)_2Sn.C_7H_8$ **3**	81.0	197.1-198.6	45.90 (46.61)	4.42 (4.32)	7.48 (7.50)	15.73 (15.88)
$[\{3,5\text{-}(NO_2)_2C_6H_3COO(C_4H_9)_2Sn\}_2O]_2.(C_7H_8)_2$ **4**	90.0	210.3-210.9	43.63 (44.61)	4.53 (5.06)	5.61 (5.62)	23.25 (23.83)
$3,5\text{-}(NO_2)_2C_6H_3COO(C_6H_5)_3Sn$ **5**	79.3	174.4-175.2	53.48 (53.51)	2.85 (3.23)	4.95 (5.00)	21.08 (21.15)

Calculated values are given in parenthesis.

TABLE-2
SELECTED INFRARED DATA OF ACIDS, SODIUM SALTS AND COMPLEXES **1-5**

Compounds	Wavelength (cm^{-1})					
	ν(OH)	$\nu(COO)_{as}$	$\nu(COO)_s$	Δν	ν (Sn-O)	ν(Sn-O-Sn)/ν(O-Sn-O)
$2,4\text{-}(NO_2)_2C_6H_3COOH$	2882-2535	1723	1346	377	–	–
$2,4\text{-}(NO_2)_2C_6H_3COONa$	–	1569	1342	227	–	–
1	–	1659, 1539	1346, 1376	313, 163	475	636
2	–	1599	1345	254	453	–
$3,5\text{-}(NO_2)_2C_6H_3COOH$	2884-2465	1701	1348	358	–	–
$3,5\text{-}(NO_2)_2C_6H_3COONa$	–	1624	1346	278	–	–
3	–	1629	1345	284	467	684
4	–	1633, 1550	1342, 1400	291, 150	477	632
5	–	1655	1343	312	444	–

$2,4\text{-}(NO_2)_2C_6H_3COONa$ = sodium salt of 2,4-dinitrobenzoic acid; $3,5\text{-}(NO_2)_2C_6H_3COONa$ = sodium salt of 3,5-dinitrobenzoic acid; $\Delta\nu = [\nu(COO)_{as} - \nu(COO)_s]$.

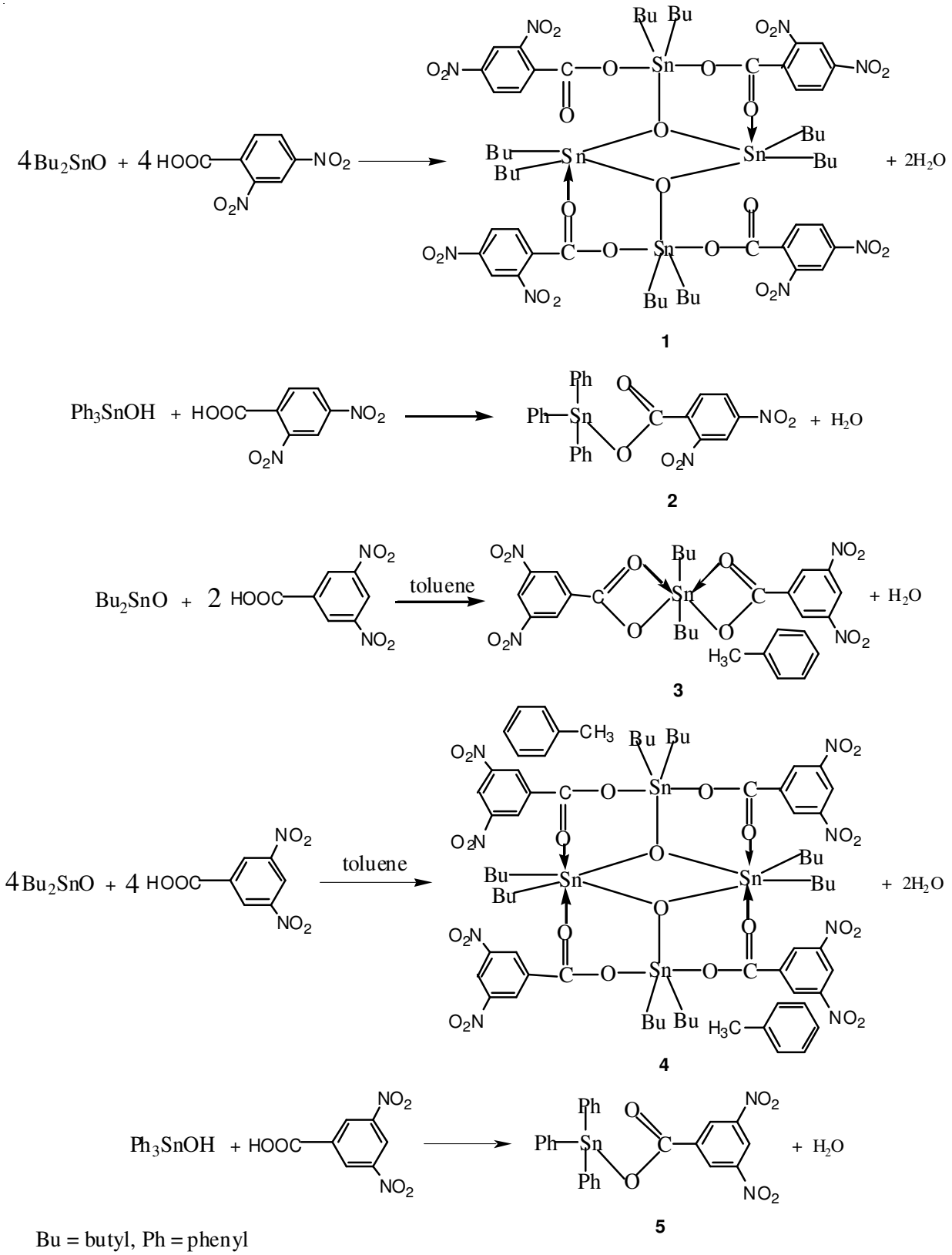


Fig. 1. Proposed reactions and structure for complexes **1-5**

2 and **5** exhibited the $\delta(^{119}Sn)$ values at -81.04 and -85.02 ppm, respectively indicating that the tin atoms were four-coordinated and have a distorted tetrahedral geometry.

The preliminary *in vitro* antibacterial screening activity of acids and complexes **1-5** are given in Table-5. Inhibition zones with a diameter less than 10 mm are considered as weak; larger than 10 mm but less than 16 mm are considered as moderate and finally larger than 16 mm and above are active[19,20]. Between complexes **1** and **2** which were both derivatives of 2,4-dinitrobenzoic acid, complex **2** was found to be inactive against *Klebsiella pneumoniae* and *Pseudomonas aeruginosa* bacterial strains. However, the antibacterial activity of

TABLE-3
^{1}H NMR DATA OF ACIDS AND COMPLEXES **1-5**

Compounds	Chemical shift, δ (ppm)		
	Benzene	Sn-R (R= Bu and Ph)	Toluene
2,4-$(NO_2)_2C_6H_3COOH$ (d_6-DMSO)	8.09 (d, 8.5 Hz, 1H) H6 8.57 (dd, 2.2 Hz, 8.4 Hz, 1H) H5 8.76 (d, 2.2 Hz, 1H) H3	–	–
1 ($CDCl_3$)	7.85 (d, 7.7 Hz, 4H) H6 8.56 (d, 6.9 Hz, 4H) H5 8.75 (s, 4H) H3	0.90 (t, 7.3 Hz, 12H) Hd 0.95 (t, 7.4 Hz, 12H) Hd 1.32-1.51 *(m, 32H) Hb and Hc 1.67-1.85 *(m, 16H) Ha	–
2 ($CDCl_3$)	7.91(d, 8.4 Hz, 1H) H6 8.36 (dd, 2.2 Hz, 8.4 Hz, 1H) H5 8.60 (d, 2.1 Hz, 1H) H3	7.47-7.50 *(m, 9H) Hm and Hp 7.75-7.78 *(m, 6H) Ho	–
3,5-$(NO_2)_2C_6H_3COOH$ (d_6-DMSO)	8.85 (d, 2.3 Hz, 2H) H2 and H6 8.99 (t, 2.2 Hz, 1H) H4	–	–
3 ($CDCl_3$)	9.27 (t, 2.2 Hz, 2H) H4 9.29 (d, 2.1 Hz, 4H) H2 and H6	0.97 (t, 7.5 Hz, 6H) Hd 1.50 (sx, 7.3 Hz, 4H) Hc 1.82 (qn, 7.4 Hz, 4H) Hb 1.99 (t, 8.2 Hz, 4H) Ha	CH_3; 2.36 (s, 3H) CH_2; 7.13-7.17 *(m, 3H) CH_2; 7.23-7.27 *(m, 2H)
4 ($CDCl_3$)	9.20 (s, 12H) H2, H4 and H6	0.83 (t, 7.1 Hz, 12H) Hd 0.96 (t, 6.2 Hz, 12H) Hd 1.36-1.48 *(m, 16H) Hc 1.81-2.03 *(m, 32H) Ha and Hb	CH_3; 2.37 (6H, s) CH_2; 7.14-7.19 *(m, 6H) CH_2; 7.24-7.31 *(m, 4H)
5 ($CDCl_3$)	9.16 (t, 2.2 Hz, 1H) H4 9.21 (d, 2.1 Hz, 2H) H2 and H6	7.49-7.55 *(m, 9H) Hm and Hp 7.79-7.83 *(m, 6H) Ho	–

s = singlet, d = doublet, t = triplet, qn = quintet, sx = sextet, dd = doublet of doublet, m = multiplet; *o* = *ortho*, *m* = *meta*, *p* = *para*. Coupling constant = Hz, * = overlap.

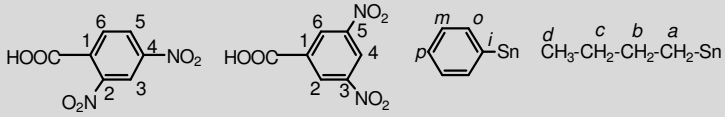
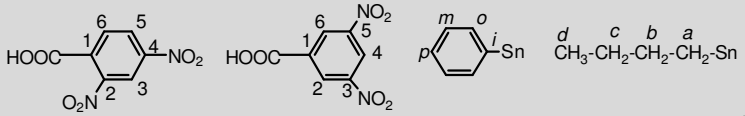


TABLE-4
^{119}Sn AND ^{13}C NMR DATA OF ACIDS AND COMPLEXES **1-5**

Compounds	Chemical shift (ppm)				
	^{119}Sn	Benzene	Sn-R (R= Bu and Ph) $^nJ(^{119}Sn\text{-}^{13}C)$ (n=1, 2, 3 and 4)	Toluene	COO
2,4-$(NO_2)_2C_6H_3COOH$ (d_6-DMSO)	–	120.25 (C3), 128.66 (C1), 132.25 (C5), 133.52 (C6), 148.75 (C2), 149.56 (C4)	–	–	165.56
1 ($CDCl_3$)	-190.69 -193.80	119.47 (C3), 127.21 (C1), 130.59 (C5), 135.62 (C6), 148.04 (C2), 148.44 (C4)	13.56 (C*d*), 13.60 (C*d*), 26.73 (C*c*), 26.96 (C*c*), 27.38 (C*b*), 27.52 (C*b*), 28.47 (C*a*), 29.63 (C*a*)	–	168.56 169.67
2 ($CDCl_3$)	-81.04	119.58 (C3), 127.26 (C1), 132.21 (C5), 134.58 (C6), 148.73 (C2), 148.97 (C4)	137.68 (^1J = 655.6 Hz) (C*i*), 137.27 (^2J = 48.9 Hz) (C*o*), 129.66 (^3J = 65.1 Hz) (C*m*), 131.17 (^4J = 13.1 Hz) (C*p*)	–	168.56
3,5-$(NO_2)_2C_6H_3COOH$ (d_6-DMSO)	–	122.82 (C4), 129.66 (C2 and C6), 135.01 (C1), 149.16 (C3 and C5)	–	–	164.68
3 ($CDCl_3$)	-127.78	122.92 (C4), 130.55 (C2 and C6), 134.78 (C1), 149.09 (C3 and C5)	13.87 (C*d*) 26.17 (C*c*), 26.83 (C*b*), 27.10 (C*a*)	21.82 125.66, 128.59, 129.39, 138.23	171.47
4 ($CDCl_3$)	-194.27 -203.44	122.20 (C4), 129.96 (C2 and C6), 137.22 (C1), 149.13 (C3 and C5)	13.87 (C*d*), 13.96 (C*d*) 27.15 (C*c*), 27.79 (C*c*), 27.99 (C*b*) 28.28 (C*b*), 29.85 (C*a*), 31.11 (C*a*)	21.76 125.65, 128.57, 129.38, 138.21	168.82
5 ($CDCl_3$)	-85.02	122.27 (C4), 129.68 (C2 and C6), 135.73 (C1), 148.86 (C3 and C5)	137.40 (^1J = 644.5 Hz) (C*i*), 137.30 (^2J = 48.9 Hz) (C*o*), 130.68 (^3J = 64.8 Hz) (C*m*), 131.26 (^4J = 13.1 Hz) (C*p*)	–	168.10



triphenyltin(IV) (complex **2**) was found to be more active compared to the dibutyltin(IV) (complex **1**) based on the screening bioassays against *Bacillus subtilis* and *Staphylococcus aureus* bacterial strains. In addition, in this series of study,

TABLE-5
PRELIMINARY *IN VITRO* ANTIBACTERIAL SCREENING ACTIVITY OF ACIDS AND COMPLEXES **1-5**

Complexes	Inhibition zone (mm)				
	Bacillus subtilis	*Escherichia coli*	*Klebsiella pneumoniae*	*Pseudomonas aeruginosa*	*Staphylococcus aureus.*
2,4-$(NO_2)_2C_6H_3COOH$	15	11	12	17	19
1	13	12	10	9	12
2	16	9	-	-	19
3,5-$(NO_2)_2C_6H_3COOH$	17	11	10	14	21
3	15	13	11	11	14
4	11	11	10	9	24
5	13	10	8	-	10
*Chloramphenicol	29	-	23	34	30
*Doxycycline	34	24	21	40	28
*Rifampicin	25	24	23	29	37

Agar well diffusion method (*in vitro*) = 1.0 mg/mL; * = Reference drug.

there were some reversed results; complex **1** was found to have more active compared to complex **2** based on the inhibition zone diameter obtained upon screening against *Escherichia coli*. This phenomenon was also detected in the *in vitro* antibacterial studies of complexes **3-5** against the tested bacterial strains. This contradicts with the fact that the increase in the number of organo groups enhances the biological activity of organotin(IV) complexes[21,22]. This phenomenon indicated that the ligands (carboxylate anions) may play an important role *in vitro* antibacterial activity[22-25].

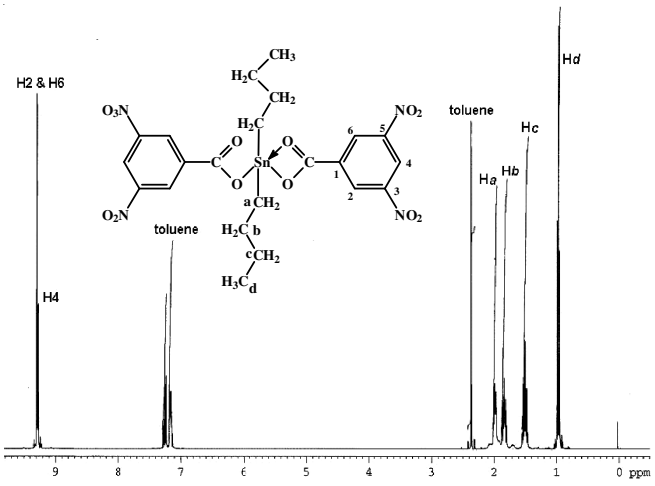


Fig. 2. ^{1}H NMR spectrum of complex **3**

Conclusion

Complexes **1-5** have been successfully synthesized and characterized quantitatively and qualitatively. Based on the preliminary *in vitro* antibacterial screening activity, all the complexes obtained showed some moderate and selective activity against the tested bacterial strains.

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REFERENCES

1. S.J. Blunden, P.A. Cusack and R. Hill, The Industrial Uses of Chemicals, Whitstable Litho Ltd., Great Britian (1985).
2. M. Gielen, M. Biesemans, D.D. Vos and R. Willem, *J. Inorg. Biochem*., **79**, 139 (2000).
3. S. Mahmood, S. Ali, M.H. Bhatti, M. Mazhar, R. Iqbal, K.M. Khan and G.M. Maharvi, *Turk. J. Chem*., **27**, 656 (2003).
4. S. Mahmood, S. Ali, M.H. Bhatti, M. Mazhar, K. Shahid, K.M. Khan and G.M. Maharvi, *Turk. J. Chem*., **28**, 17 (2004).
5. M.N. Xanthopoulou, S.K. Hadjikakou, N. Hadjiliadis, E. Milaeva, J.A. Gracheva, V.Y. Tyurin, N. Kourkoumelis, K.C. Christoforidis, A.K. Metsios, S. Karkabounas and K. Charalabopoulos. *Eur. J. Med. Chem*., **43**, 327 (2008).
6. M. Hanif, M. Hussain, S. Ali, M.H. Bhatti, M.S. Ahmed, B. Mirza and H. Stockli-Evans, *Polyhedron*, **29**, 613 (2010).
7. Y.-F. Win, S.-G. Teoh, S.-T. Ha and T.-S. Tengku-Muhammad *Afr. J. Biotechnol.*, **11**, 13140 (2012).
8. R. Zhang, J. Sun and C. Ma, *J. Organomet. Chem*., **690**, 4366 (2005).
9. Y.F. Win, S.G. Teoh, N.L. Ismail and B.M. Yamin, *Acta Cryst*., E**62**, m3146 (2006).
10. Y.F. Win, S.G. Teoh, J.B.J. Teh, H.K. Fun and L. Zakaria, *Acta Cryst*., E**63**, m323 (2007).
11. Y.-F. Win, S.-G. Teoh, S.-T. Ha, T.-S. Tengku-Muhammad and E. Yousif, *Asian J. Chem*., **25**, 3376 (2013).
12. Y.F. Win, S.G. Teoh, E.K. Lim, S.L. Ng and H.K. Fun, *J. Chem. Crystallogr*., **38**, 345 (2008).
13. Y.F. Win, C.-S. Choong, S.-T. Ha, C.K. Quah and H.-K. Fun, *Acta Cryst*., E**67**, m535 (2011).
14. Y.F. Win, C.-S. Choong, S.-G. Teoh, C.K. Quah and H.-K. Fun, *Acta Cryst*., E**67**, m1276 (2011).
15. M. Danish, M.N. Tahir, S. Ghafoor, N. Ahmad, S. Ali and E.R.T. Tiekink, *J. Chem. Crystallogr*., **41**, 1365.
16. J. Holecek, M. Nadvorník, K. Handlír and A. Lycka, *J. Organomet. Chem*., **315**, 299 (1983).
17. J. Holecek, K. Handlír, M. Nádvornik and A. Lycka, *J. Organomet. Chem*., **258**, 147 (1983).
18. J. Holecek, M. Nadvorník, K. Handlír and A. Lycka, *J. Organomet. Chem*., **241**, 177 (1983).
19. Y.-F. Win, S.-G. Teoh, M.R. Vikneswaran, S.-T. Ha and I. Pazilah, *Int. J. Phys. Sci*., **5**, 1263 (2010).
20 Z.H. Chohan, M. Arif, M.M. Akhtar and C.T. Supuran, *Bioinorg. Chem. Appl.*, 1 (2006).
21. S.-U. Rehman, S. Ali, M. Mazhar, A. Badshah and M. Parvez, *Heteroatom Chem*., **17**, 420 (2006).
22. S.-U. Rehman, K. Shahid, S. Ali, M.H. Bhatti and M.Parvez. *J. Organomet. Chem*., **690**, 1396 (2005).
23. S.-U. Rehman, K. Shahid, S. Ali, M. Mazhar, A. Badshah, G. Eng, X. Song and J. Ryczkowski, *Heteroatom. Chem*., **16**, 175 (2005).
24. M. Nath, R. Yadar, G. Eng, T.-T. Nguyen and A. Kumar, *J. Organomet. Chem.,* **577**, 1 (1999).
25. M. Nath, R. Jairath, G. Eng, X. Song and A. Kumar, *Spectrochim. Acta A,* **62**, 1179 (2005).