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Research Article

CHEMISTRY

Supramolecular design and biological activity of coordination polymer based on dimethyltin (IV) and N-donor ligand

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Abstract:

The supramolecular polymer of the type [Me_2SnCl_2L], 1, L = 2,2'-bipyridine (2,2'-bpy), has been synthesized by the reaction of dimethyltin (IV) dichloride and 5-nitroisophthallic acid in the presence of sodium ethoxide and 2,2'-bpy. The compound was structurally characterized by elemental analysis, FT-IR spectra and X-ray single crystal. The x-ray data exhibited 1:1 stoichiometry for the dimethyltin dichloride: 2,2'-bpy ligands. The structure of 1 extends along the a-axis in a parallel way forming 1D-chains via H-bonds while they further propagate creating 2D- network via extensive H-bonds. The biological activity against some fungi and bacterial microorganisms has been also studied.

Introduction:

Supramolecular chemistry is concerned with preparing assemblies of molecules using a combination of secondary chemical interactions rather than covalent bonding [1-3]. The comparatively simple molecules used in these assembles are driven to spontaneously self-assemble, and then hold together, via such non-covalent interactions as hydrogen bonds, metal–ligand coordination interactions and π-π stacking. [4-7]. Self-assembly has long been known: Fischer's lock-and-key theory of enzyme activity may be considered as their foundation store because it recognized the central role of shape and geometry in molecular interactions. Organotin (IV) compounds form an important series of compounds and have been receiving increasing attention in recent years [8-14]. Investigations have been carried out to test their antitumor activity and it has been observed that indeed several diorganotin adducts show potentials antineoplastic, antituberculotic agents, bioactivities, in particular as potential biocidal (e.g., antimicrobial, antifungal) [15-17]. In this paper, we report the synthesis crystal structure and biological activities of dimethyltin (IV) polymer of the type [Me2SnCl2.(2,2'-bipy)]n.

2. Experimental

2.1. Materials and Methods

All reagents were purchased from Aldrich and used without further purification. Infrared spectra from 4000–400 cm^{-1} were recorded on a BRUCKER FT-IR instrument, using KBr pellets. Microanalyses (C, H, N) were carried out with a Perkin-Elmer 2400 automatic elemental analyzer. Structural measurements were performed on a Kappa CCD Enraf-Nonius FR590 four circle goniometer with graphite monochromatic MoKα radiation source (λ = 0.71073 A°) at 25 ± 2 °C and 20 mA/50 kV.

2.2. X-Ray Crystallography and Structure Determination.

The well-developed crystal was mounted on glass fibers, and the measurements were made at 25 ± 2 °C. The structure was solved using direct-methods and all of the non-hydrogen atoms were located from the initial solution or from subsequent electron density difference maps during the initial stages of the refinement. After locating all of the non-hydrogen atoms in the structure, the model was refined against F^2, first using isotropic and finally anisotropic thermal displacement parameters. The positions of the hydrogen atoms were then calculated and refined isotropically, and a final cycle of refinements was performed.

2.3. Preparation of [Me_2SnCl_2.(2,2'-bipy)]n,1

The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. A solution of 5-nitroisophthalic acid (0.211 g, 1.0 mmol) in methanol was added to a solution of sodium ethoxide (0.136 g, 2.0 mmol) in methanol. The mixture was stirred for 10 min, then added to a mixture of 2,2'-bipy (0.3124 g, 2.0 mmol) and dimethyltin (IV) dichloride (0.44 g, 2.0 mmol) in methanol. The reaction has been continued about 12 h at 40 °C.

After cooling down to the room temperature, the solution was filtered. Already, after 3 weeks, colorless crystals started growing from the initially clear filtrate. After filtration, washing with small quantities of methanol and overnight drying, colorless crystals were obtained. Yield: 70%. MP 220–225 °C. Anal. Calcd. for ($C_{12}H_{14}Cl_2N_2Sn$) MW = 375.854 g mol^{-1}: C, 38.35; H, 3.75; N, 7.45; Cl, 18.86; Sn, 31.58. Found: C, 38.41; H, 3.70; N, 7.38; Cl, 18.82; Sn, 31.53.

2.4. Biological Activities

Disc diffusion method recorded by Pridham et al. [18] was employed to determine the antimicrobial activity. Freshly prepared spore suspension of different test microorganisms (0.5 mL of about 10^6 cells/mL) was mixed with 9.5 ml of melting sterile Sabouraud's dextrose medium (for fungi) or nutrient agar medium (for bacteria) at 45°C, poured on sterile Petri dishes, and left to solidify at room temperature.

Regular cellulose filter paper discs of 6 mm diameter were prepared under aseptic conditions. Each disc was saturated with 20 mg of each tested suspended material. Three replicas were made for each test, and all plates were incubated at 27°C for 48 hours for fungi, and at 32°C for 24 hours for bacteria. Then the average diameters of inhibition zones were recorded in millimeters, and compared for all plates.

3. Results and Discussion

The reaction of the ternary adducts dimethyltin (IV) dichloride and 5-nitroisophthallic acid in the presence of sodium ethoxide and 2,2'-bipyridine in methanol under nitrogen atmosphere at 40 ^oC affords colorless cubic crystals of the mono nuclear and mono-ligand adduct of the empirical composition [Me_2SnCl_2.(2,2'-bpy)],1. Many trials had been carried out to coordinate 5-nitroisophthallic acid to the tin atom which ended up so far unsuccessfully. The lattice constants, density and refinement parameters of 1 are collected in Table (1), while the intermolecular bond lengths and bond angles are collected in Table (2).

The cell unit comprises the formula [Me_2SnCl_2 (2,2'-bpy)] exhibiting Z = 4 and atom size occupancy 1 confirming the

assignment of 1:1 stoichiometry for the dimethyltin dichloride: 2,2'-bipyridine ligand.

Table (1): Crystal data and structure refinement parameters of **1**

Parameters	**1**
Empirical Formula	$C_{12}H_{14}Cl_2N_2Sn$
Formula Weight g/mol	375.854
Temperature (K)	298
Crystal system	Monoclinic
Space group	C 2/c
a/Å	6.6364 (2)
b/Å	17.0155 (7)
c/Å	13.2220 (5)
α/°	90.00
β/°	104.429 (2)
γ/°	90.00
V/Å^3	1445.96 (9)
Z	4
μ(Mo-Kα)/m.m^{-1}	2.12
Calculated density/mg. m^{-3}	1.727
Goodness-of-fit on F^2	0.9525
F(000)	864
R indices[I>3σ(I)] R1/wR2	0.0361/ 0.0898
R indices (all data)	0.069/ 0.114
R_{int}	0.047
Data/restraints/parameters	1595/0/78

Table (2): Bond lengths (Å) and bond angles (deg.) of **1**

Bond lengths (Å)		Bond angles (deg.)	
Sn1-N3	2.400(3)	N3-Sn1-Cl2	162.10(10)
Sn1-Cl2	2.5348(12)	N3-Sn1-C9	87.66(19)
Sn1-C9	2.124(4)	Cl2-Sn1-C9	92.21(16)
Sn1-Cl2	2.5348(12)	N3-Sn1-Cl2	93.07(10)
Sn1-N3	2.400(3)	Cl2-Sn1-Cl2	104.84(6)
Sn1-C9	2.124(4)	C9-Sn1-Cl2	90.53(15)
N3-C4	1.333(6)	N3-Sn1-N3	69.03(19)
N3-C8	1.355(5)	Cl2-Sn1-N3	93.07(10)
C4-C5	1.380(7)	C9-Sn1-N3	88.64(18)
		Cl2-Sn1-N3	162.10(10)
		N3-Sn1-C9	88.64(18)
		Cl2-Sn1-C9	90.53(15)
		C9-Sn1-C9	175.5(3)
		Cl2-Sn1-C9	92.21(16)
		N3-Sn1-C9	87.66(19)
		Sn1-N3-C4	122.0(3)
		Sn1-N3-C8	118.1(3)

In this case the asymmetric unit cell of 1 contains, simply, one dimethyltin dichloride and one 2,2'-bipyridine molecules (Fig. 1). The Sn atom has an identity symmetry operation with the symmetry transformation X, Y, Z while the Cl(2) atom has inversion center symmetry operation with inversion at [0,0,0]. The N(3) and C(8) atoms locate at centering vector symmetry operation with centering vector [1/2,1/2,0] and at 2 fold-screw axis with direction [0,1,0] at 1/4,y,1/4 with screw component [0,1/2,0], respectively.

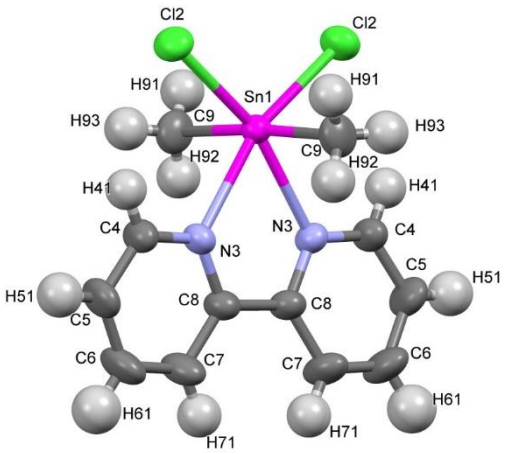

Figure (1): Asymmetric unit of **1** showing the atom labeling scheme and thermal ellipsoids are shown 50% probability.

The tin center displays distorted octahedral coordination geometry formed by coordination of the two nitrogen atoms of the 2,2'-bpy and two Cl atoms in equatorial plane in addition to two methyl ligands in axial positions. The Sn–N bond lengths [2.40 Å] are apparently longer than the Sn–C bond lengths [2.124 Å] while the Sn-Cl bond lengths are much longer [2.535 Å]. The axial C9-Sn1-N3 and C9-Sn1-Cl2 angles are 87.64 and 90.53^o, respectively and the four donor atoms on the equatorial plane are perfectly planar. The smallest equatorial bond angle is observed for N(3)–Sn(1)–N(3) (69.03^o) while the other equatorial bond angles equal to 93.7^o and 104.84^o. The two pyridyl rings are not planar exhibiting a dihedral angle of 12.87^o. The structure of 1 extends along the a-axis in a parallel way forming 1D-chains via H-bonds (Fig. 2). The Sn–Sn distance in the chain is 9.132 Å while the Sn–Sn distance between two chains is 6.636 Å. On the other hand, the structure propagates along the c-axis or in ab-plane creating parallel rows which are connected by H-bonds forming 2D-network (2.690-2.961 Å). The hydrogen

bonds represent the only supramolecular interaction in the structure of 1.

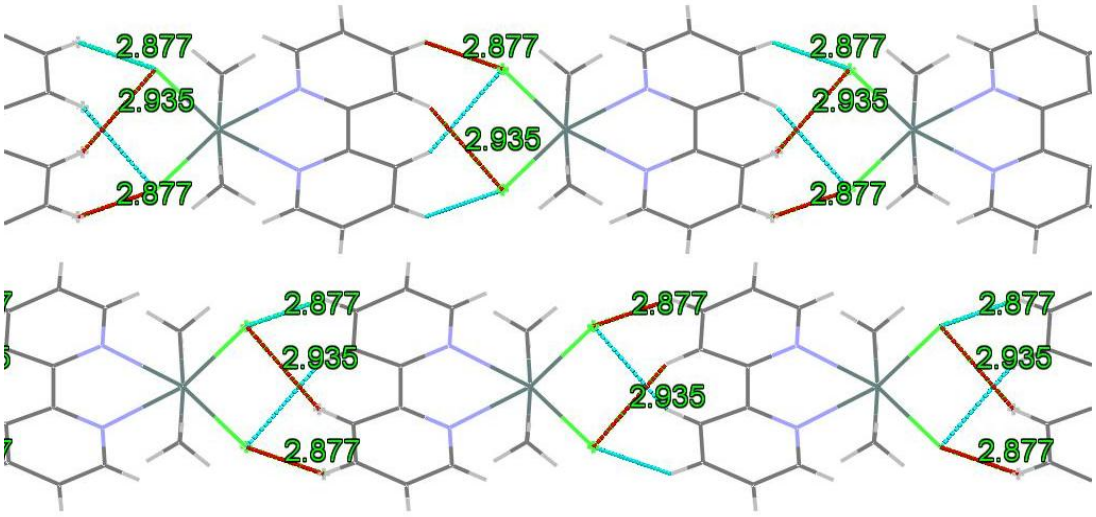

Figure (2): A view of the network structure of **1**, showing the 1D-chains along the a-axis.

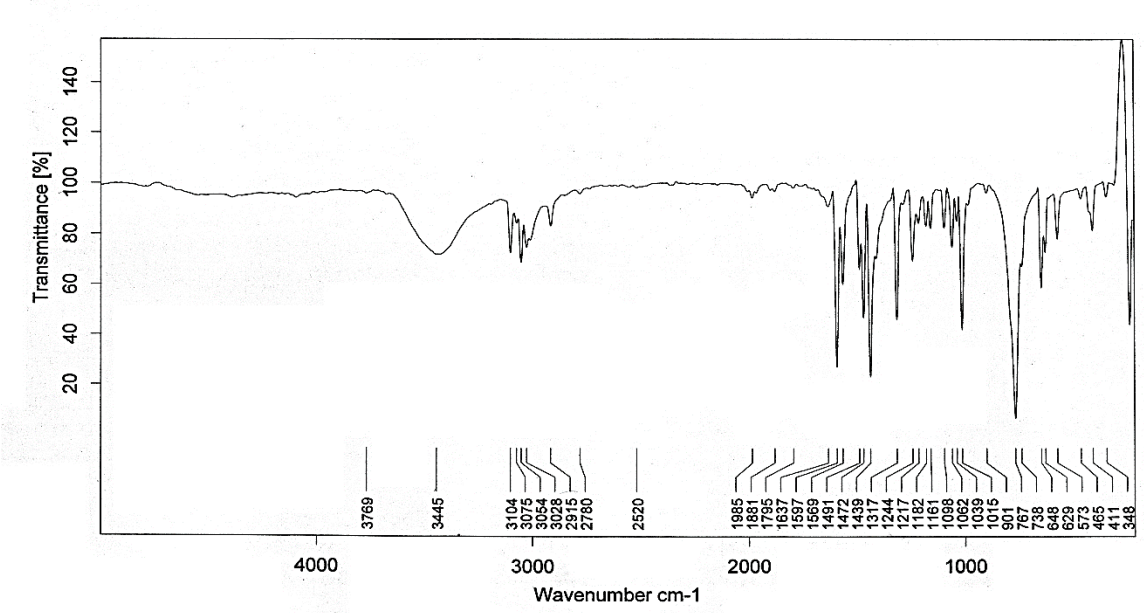

Figure (3): IR spectrum.

3.1. IR spectra

The presence of the aromatic systems was confirmed by IR spectra (Fig. 3), which displays the stretching frequencies of interest. The medium and weak bands at 3104, 3054 and 3028 cm^{-1} are attributed to $\nu_{CH(arom)}$. The aromatic ring stretching vibrations involving $\nu_{(C=N)}$ and $\nu_{(C=C)}$ appear as medium intense bands at 1597 and 1439 cm^{-1}, respectively. The $\nu_{(C=N)}$ band exhibits slightly shift than that of the free ligand supporting the coordination of 2,2'-bipyridine to the Sn(IV). The intense bands in the region of 1317 cm^{-1} and 648-767 cm^{-1} are assigned to δ_{CH} and $\gamma_{CH,}$ respectively. Also, the IR spectrum shows the stretching vibrations of Sn-C bond that appears as a medium band at 573 cm^{-1}. The medium bands at 2915-2890 cm^{-1} correspond to $\nu_{CH(aliphatic)}$ of methyl groups, supporting the presence of the dimethyltin units. On the

other hand, the stretching vibrations of Sn-N bond appears at 465 573 cm^{-1}, confirming the coordination from 2,2'-bipyridine nitrogen atom to Sn.

3.2. Antimicrobial assessment

Screening the antimicrobial activity of the tested organoltin (IV) coordination polymer showed moderate inhibitory action, giving inhibition zone diameters of 1.8 cm against Aspergillus niger and 1.7cm against Pseudomonas aeruginosa, that were followed by 1.6 cm against Fusarium oxysporum and 1.5 cm against Staphylococcus aureus as shown in Table (3).

Table (3): Diameters of inhibition zone (cm) of tested compound against different species of microorganisms.

Microorganism	Inhibition zone (cm)
Candida albicans	0.9
Cryptococcus neoformans	1.1
Aspergillus niger	**1.8**
Fusarium oxysporum	**1.6**
Escherichia coli	1.1
Staphylococcus aureus	**1.5**
Pseudomonas aeruginosa	**1.7**
Salmonella typhi	1.2

These findings were confirmed by the determination of the minimum inhibitory concentration (MIC) for the most affected microorganisms against the tested dimethyltin (IV) coordination polymer, as higher antimicrobial activity can be proved by low MIC values, recording 12.5 mg/ml as a low, highly effective MIC value against both Aspergillus niger and Pseudomonas aeruginosa, that was followed by MIC of 25 mg/ml against Fusarium oxysporum and Staphylococcus aureus.

References

1. *J.-M. Lehn, Supramolecular Chemistry — Concepts and Perspectives, VCH, Weinheim, 1995.*
2. *J.-M. Lehn, Chem. Eur. J.,1999, 5, 2455.*
3. *R. H. Wang, L. Han, L.J. Xu, Y.Q. Gong, Y.F. Zhou, M.C. Hong, A.S.C. Chan, Eur. J. Inorg. Chem., 2004, 2004(18), 3751.*
4. *M. L. Tong, S. L. Zheng, X. M. Chen, Polyhedron, 2000, 19(15), 1809.*
5. *C. H. Yan, T. L. Zhang, J. G. Zhang, G J. Yu, Struct. Chem., 2006, 17(4), 445.*
6. *C. Janiak, Dalton Trans., 2003, 14, 2781.*
7. *M. Dua, C.-P. Li, C.-S. Liu, S.-M. Fang, Coordination Chemistry Reviews, 2013, 257, 1282.*
8. *R. García-Zarracino, H. HÖpfl, Angew. Chem. 116 (2004) 1533 Angew. Chem., Int. Ed. Engl., 2004, 43, 1507.*
9. *R. García-Zarracino, H. HÖpfl, J. Am. Chem. Soc., 2005, 127, 3120.*
10. *Naqeebullah Khan, Yang Farina, Lo Kong Mun, Nor Fadilah Rajab, Normah Awang, Polyhedron 2015, 85, 754.*
11. *T.P. Lockhart, Organometallics, 1988, 7, 1438.*
12. *G. Prabusankar, R. Murugavel, Organometallics, 2004, 23, 5644.*
13. *S.W. Ng, V.G.K. Das, G. Pelizzi, F. Vitali, Heteroatom Chem.,1990, 1, 433.*
14. *Shabbir Hussain, Saqib Ali, Saira Shahzadi, Muhammad Nawaz Tahir, Muhammad Shahid, Khurram Shahzad Munawar, Syed Mustansar Abbas, Polyhedron, 2 016, 117 (15) 64.*
15. *Khodayar Gholivand, Ali Asghar EbrahimiValmoozi, Akram Gholami, Michal Dusek, Vaclav Eigner, Sara Abolghasemi, J. Organom. Chem., 2016, 806, 33.*
16. *A. Chaudhary, M. Agarwal, R.V. Singh, Appl. Organomet. Chem., 2006, 20, 295.*
17. *A. Chaudhary, R.V. Singh, Main Group Met. Chem., 2008, 31, 107.*
18. *T. G. Pridham, L. S. Lindenfesler, O. L. Shotwell, F. H. Stodola, R. G. Bendict, P. Jacks W. Zaumeyer, W. Perston and J. Mitchell. Antibiotics against plant disease: A laboratory and green house survey. Phytopathology, 1956, 46, 568.*