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Novel binuclear diorganotin(IV) complexes of adipic acid dihydrazone containing flexible aliphatic spacer: X-ray structural characterization of dimethyltin(IV) complex

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ABSTRACT

Three novel binuclear diorganotin(IV) derivatives formulated as $(R_2Sn)_2L$ (where R = Me, Bu and Ph) of a new symmetrical adipodihyrazone ligand, 1,6-bis(5-hydroxy-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)hexane-1,6-dione (H_4L) derived from the Schiff base condensation of adipic acid dihydrazide and benzoylacetone in a 1:2 M ratio were synthesized. The micro-analysis and various spectroscopic techniques viz., infrared (IR), multinuclear (^1H, ^{13}C and ^{119}Sn) magnetic resonance (NMR) spectroscopy and electrospray ionization mass (ESMS) spectrometry were employed to establish the chelating mode of the dihyrazone ligand towards the diorganotin moieties $[R_2Sn(IV)]^{2+}$. The single crystal X-ray diffraction analysis of complex, $(Me_2Sn)_2L$ reveals that it crystallizes in monoclinic space group 'P 2_1/n' and consists of crystallographically discrete molecules. The complex has been investigated to prefer a highly distorted trigonal-bipyramidal geometry (TBP) over the square-pyramidal geometry (SP) around each tin centre wherein the more electronegative enolic and benzoylic oxygen atoms of the ligand are aligned axially, and two carbon atoms of the methyl groups attached to the tin metal atom and the imine nitrogen atom of the ligand aligned themselves equatorially around the tin centre in a trigonal plane. Thermal decomposition patterns of the dimethyl- and diphenyltin(IV) derivatives in air were also investigated by TG, DTG and DTA techniques.

1. Introduction

Among Schiff base ligands containing ONO donor set of atoms, acylhydrazones, built on the $-CONHNH_2$ structural moiety have been well established to exhibit fascinating chelating possibilities in their metal complexes as a result of the trigonal N- and O-donor atoms. In the last few decades, these ligands have motivated many research groups to develop and design new hydrazones and their metal complexes with a promising therapeutic activity after the synthesis of methyl pyrazinylketone isonicotinoyl hydrazones, potential chelators to cure the Fe overload disease [1]. A number of organotin(IV) complexes of various acylhydrazones have been structurally characterized, and reported to exhibit good to moderate antibacterial, antifungal and antitumor activities as compared with the standard drugs [2–8]. The structural diversity, the coordination state of the tin metal atom and number/nature of the alkyl groups attached to the tin atom are considered to be accountable for the variable biochemical activity investigated in the organotin(IV) complexes [9,10]. The organotin(IV) complexes of acylhydrazones were analyzed by single crystal X-ray diffraction crystallography and were reported to possess a trigonal-bipyramidal (TBP) or square-pyramidal geometry (SP) with a penta-coordinated tin atom [11,12]. In some of the instances, organotin(IV) complexes were found to behave as a Lewis acid and accept the electron density from solvent molecules and other molecules with donor atoms, and in this way resulting in a pentagonal-bipyramidal geometry with a seven coordinated tin atom [13,14]. There are also a few reports on organotin(IV) complexes wherein the molecules are self-assembled by the intramolecular O-H ··· X or C-H ··· X (X = O or N) hydrogen bonding interactions [15,16]. Despite of the several reports on the organotin(IV) complexes of acylhydrazones [17], a few organotin(IV) complexes of bis-acylhydrazones with two sets of ONO donor atoms have been investigated, and tested for their biological activities against the standard drugs [18–22]. Moreover, a bis-acylhyrazone may afford varying number of donor atoms and so

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exhibit different types of coordination modes viz., monobasic bis-bidentate, monobasic bis-tridentate or dibasic bis-tridentate or may afford polymerization [22]. The varying degree of flexibility in the aliphatic chains connecting the two coordinating units can tailor supramolecular architectures such as double helices, grids, racks or coordination polymers [23]. In view of the little work on the diorganotin(IV) complexes of bis-acylhydrazones reported in the literature, and their unique chelating ability towards the organotin(IV) moieties, we were motivated to explore the coordination chemistry of diorganotin(IV) complexes of adipodihyrazone. In the present work, we have reported the synthesis and characterization of a new adipodihyrazone, 1,6-bis(5-hydroxy-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)hexane-1,6-dione (H_4L) containing a flexible butylene linker (Fig. 1) and its corresponding three novel diorganotin(IV) derivatives formulated as $(R_2Sn)_2L$ (where R = Me, Bu and Ph) in the presence of a proton abstractor, triethylamine. The single crystal X-ray diffraction crystallographic analysis of dimethyltin(IV) complex, $(Me_2Sn)_2L$ has also been performed.

2. Experimental

2.1. Materials

Dimethyltin(IV) dichloride (Sigma Aldrich), di-*n*-butyltin(IV) oxide (Sigma Aldrich), diphenyltin(IV) dichloride (Sigma Aldrich) were commercially procured. Adipic acid dihydrazide (Sigma Aldrich), benzoylacetone (Hi-Media), and triethylamine (AR grade, Rankem) were used as received. Methanol (specially dried) (Fisher Scientific) was used as solvent throughout the all synthesis.

2.2. Physical measurements

Melting points of all synthesized compounds were recorded on an OptiMelt Automated Melting Point System, Digital Image Processing Technology, Stanford Research Systems instrument, and were uncorrected. Micro-analysis for the percentage of elemental contents (C, H and N) in all studied compounds was carried out on a Vario Micro CHNOS Elemental analyzer instrument. For IR spectra, all compounds as KBr dics were scanned in the IR frequency range of 4000–400 cm^{-1} on a Nicolet 6700 Nexus FT-IR Spectrophotometer. All multi-nuclear (^1H, ^{13}C, and ^{119}Sn) magnetic resonance spectra were run in a non-coordinating NMR solvent ($CDCl_3$) on a JOEL Delta (400 MHz) FT-NMR spectrometer at ambient temperature. The chemical shifts (ppm) and coupling constants (Hz) observed in the ^1H and ^{13}C NMR spectra of compounds were precisely referred to the position of residual solvent proton signal, marked at δ = 7.26 and 77.16 ppm [24], respectively. ESI (electrospray ionization) mass spectra, executed in a positive ion detection mode were acquired from SAIF, Central Drug Research Institute, Lucknow, India. Single crystal X-ray diffraction data for the compound $(Me_2Sn)_2L$ was collected on a Bruker Kappa Apex-II CCD diffractometer equipped with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) source at 293(2) K at the Institute Instrumentation Centre (IIC), Indian Institute of Technology Roorkee (IITR), Roorkee, India. The data acquisition was performed with a suitable yellow crystal of dimension 0.40 × 0.37 × 0.35 mm. The "direct method with SIR-92 programme" was employed to solve the crystal structure [25]. The "full matrix least squares method on F^2" was used to refine all non-hydrogen atoms anisotropically using SHELXL97 programme [26]. The hydrogen atoms were included at the geometrically determined positions, and were allowed to ride on their pertinent atoms. Besides, refinement of the hydrogen atoms was not carried out. Mercury, version 3.9 software was utilized to draw ORTEP and molecular packing diagrams. Thermograms of dimethyl- and diphenyltin(IV) derivatives were obtained on a Perkin-Elmer (Pyris Diamond) thermal analyzer by pyrolysis in a platinum crucible in the temperature range 28–1000 °C, in air (200 mL/min) with a controlled heating rate 5 °C/min, and by employing alumina powder as a reference material at I. I. C., IITR.

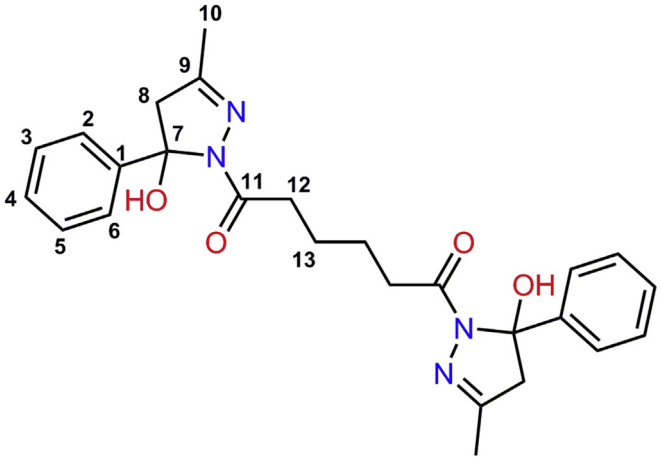

Fig. 1. Cyclic structure of hexadentate 1,6-bis(5-hydroxy-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)hexane-1,6-dione, H_4L along with the atomic labeling for NMR assignments.

2.3. Synthesis

Schiff base ligand, 1,6-bis(5-hydroxy-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)hexane-1,6-dione (H_4L), obtained from the condensation of adipic acid dihydrazide and benzoylacetone, and its substituted diorganotin(IV) derivatives were synthesized as described below:

2.3.1. Synthesis of 1,6-bis(5-hydroxy-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)hexane-1,6-dione (H_4L)

To a methanol (30 mL) solution of adipic acid dihydrazide (0.871 g, 5 mmol) was added benzoylacetone (1.62 g, 10 mmol) in methanol (20 mL) with continuous stirring. The contents were further refluxed for 5 h at ambient temperature. The ligand solidified as a creamy solid from the refluxed solution after keeping it for few days at room temperature. The creamy solid so obtained was filtered under vacuum, washed with methanol, and dried in *vacuo*.

Creamy solid; Yield: 81%; m.p. 120 °C; Anal. Calcd. for $C_{27}H_{30}N_4O_3$ (462.55): C, 67.51; H, 6.54; N, 12.11. Found: C, 67.74; H, 6.57; N, 12.51; ES-MS (*m*/*z*): 485.18 $[(C_{13}H_{15}N_2O_2)_2+Na]^+$; 463.56 $[(C_{13}H_{15}N_2O_2)_2+H]^+$; 444.79 $[(C_{13}H_{15}N_2O_2)_2+H\text{-}OH]^+$; 426.89 $[(C_{13}H_{15}N_2O_2)_2+H\text{-}2OH]^+$; 286.96 $[C_{16}H_{19}N_2O_3]^+$; Selected FT-IR Data (KBr, νmax/cm^{-1}): 3389, ν(O-H); 2967, 1451 ν(CH_2); 1635, ν(C=O)/ν(C=N)azomethine; 1324, ν(C-O); 1151, ν(OH); ^1H NMR (399.78 MHz, $CDCl_3$, δ(ppm)): 1.69 (t, 4H, H-13); 2.03 (s, 6H, H-10); 2.70 (t, 4H, H-12); 2.89 (d, 2H, H-8, $^2J_{H\text{-}H}$ = 18.7 Hz); 3.25 (d, 2H, H-8, $^2J_{H\text{-}H}$ = 18.7 Hz); 5.13 (s, br, 2H, HOC); 7.35–7.24 (m, 10H, H-2 to H-6); ^{13}C NMR (100.53 MHz, $CDCl_3$, δ(ppm)): 16.18, C-10; 24.21, C-13; 34.09, C-12; 54.16, C-8; 93.48, C-7; 123.91, C-2, C-6; 128.06, C-3, C-5; 128.79, C-4; 144.05, C-1; 154.19, C-9; 173.42 C-11.

2.3.2. Synthesis of $(Me_2Sn)_2L$, N, N-bis(4-oxy-4-phenylbut-3-en-2-ylidene)hexanedihydrazonato)tetramethyl-di-tin(IV)

To a methanol (20 mL) solution of H_4L (0.462 g, 1 mmol) was added Et_3N (0.4 g, 4 mmol) in methanol (10 mL) with continuous stirring. A methanol (20 mL) solution of Me_2SnCl_2 (0.55 g, 2.5 mmol) was added to the stirred solution, and was refluxed for