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Short communication

Synthesis and crystal structure of a novel pentanuclear complex of tin (IV) with heterocyclic sulfur and nitrogen donor ligands

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Abstract

A novel macrocyclic complex of organotin was synthesized by the reaction of dibutyltin dichloride with 2,5-dimercapto-1,3,4-thiodiazole. The title pentanuclear complex of tin is a 35-membered macrocycle. All five Sn atoms are six-coordinate, and have distorted octahedron geometries due to intramolecular Sn–N interactions. The title complex is characterized by Elemental analysis, IR, ^{1}H-NMR spectroscopy and X-ray diffraction.

Keywords: Pentanuclear complex; Macrocycle; Crystal structure

1. Introduction

Recent development in coordination chemistry has produced numerous polymers and supramolecular complexes through the election of appropriate coordination geometry of metal ions and the chemical structure of organic ligands [1]. Ligands with particular symmetry and stereochemistry have led to different specific architectures. For example, 1D linear macromolecule and infinite 2D network complex could be prepared by the reaction of metal ions with 4,4′-bipyridine or pyrimidine [2–4]. Nanometersized metallosupramolecular cube and nanometersized tube were obtained by the treatment of tpst (2,4,6-tris[(4-pydidyle)-methylsulfanyl]-1,3,5-triazine) with Ni(II) and silver(I) salts, respectively [5,6]. A bowl-like macrotricycle and a crown-like structure were also found when [Pd(NO_3)(en)] reacted with 2,4,6-tris(3-pyridine)-1,3,5-triazine and silver(I) salt with bpsb (1,2-bis[(2-pyrimidinyl)-sulfanymethyl]benzen) [7–9]. Accordingly, it is crucial to choose and design linking ligands for the construction of specific topologies.

Having symmetrical –SH groups and azole-N atoms, 2,5-dimercapto-1,3,4-thiodiazole (bismothol-I) is a good organic ligand containing both sulfur and nitrogen donors for the preparation of coordination polymers. Out of our expect to gain a one- or two-dimensional polymer by the coordination of sulfur and nitrogen atoms to tin, the reaction of 2,5-dimercapto-1,3,4-thiodiazole with dibutyltin dichloride led to a 35-membered macrocyclic complex of tin. The complex contains crown-like cavities. It is worthy to note that, since polymers have been studied so far and binuclear or trinuclear polymers are ordinary, such pentanuclear compound is still scarce. We characterized the title complex by Elemental analysis, IR, ^{1}H-NMR, X-ray diffraction and have a discussion on its' structure. The reaction equation was shown in Scheme 1.

2. Results and discussion

The bismothol I ligand possesses four bonding sites, two sulfur atoms and two nitrogen atoms. Due to the rigid symmetry of two thio-S atoms, the sulfur atoms of bismothol I ligand can only bond to different metal atoms. Therefore bismothol I may be able to bridge different metal atoms in specific directions. Figs. 1 and 2 show the molecular structure of complex (I). As

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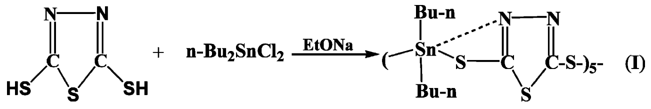

Scheme 1.

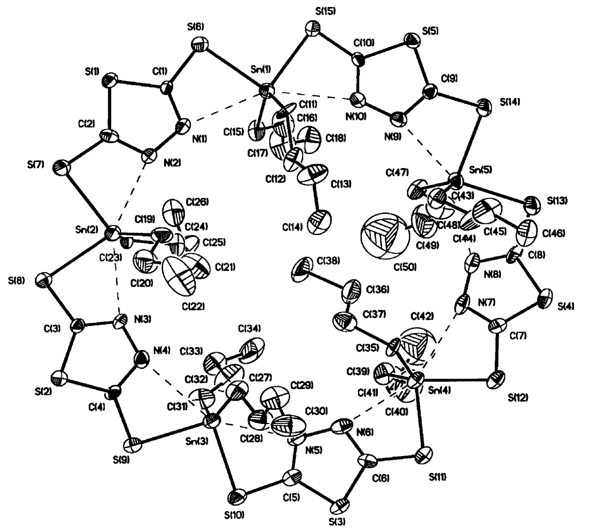

Fig. 1. Molecular structure of complex (I).

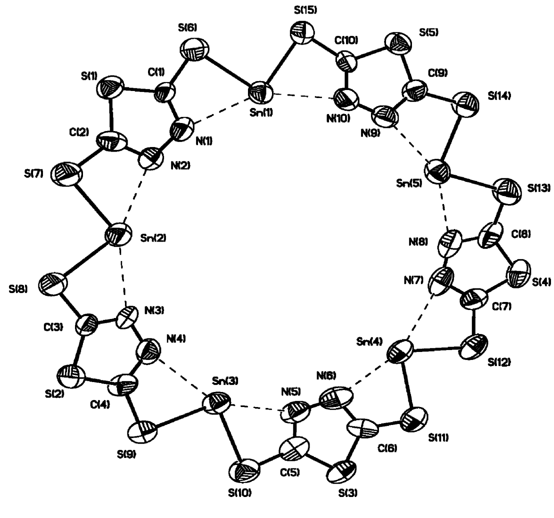

Fig. 2. Intramolecular Sn···N interactions (omitting butyl groups).

expected, each bismothol I in complex (I) functions as a tetradentate ligand, in which, as thiolate species, two sulfur atoms coordinated to two tin atoms in opposite directions to meet the linear coordination of the tin atoms and both two nitrogen atoms have weak interactions with tin atoms. The five bismothol I ligands are linked by five tin atoms and formed a 35-membered macrocycle.

The average bond distance of Sn–S (2.494 Å) is shorter than Sn–S in t-Bu$_2$Sn (S$_2$CNEt$_2$)$_2$ (2.554 Å) [10], tribenzyl(2-thiolatopyridine-N-oxide)tin (2.577 Å) [11] and the sum of the van der Waals radii of 4.0 Å [12]. It is similar to the Sn–S bond length in Ph$_3$Sn(SCN$_4$CH$_3$) (SCN$_4$CH$_3$ = 1-methyltetrazole-5-thiolate) (2.471 Å) [13], Me$_3$SnS$_2$CNMe (Sn–S 2.47 Å) [14], and close to the sum of the covalent radii of Sn and S (2.44 Å) [15], which proves that sulfur atoms coordinated to tin atoms by strong chemical bonds. The average Sn←N bond distance (2.762 Å) approach similar intermolecular Sn←N (2.787 Å) bond length in trimeric [Me$_3$SnSCN$_4$Ph]$_3$ unit [16], and is midway between the sums of the van der Waals and covalent radii of Sn and N, 3.74 and 2.15 Å [17]. The intermolecular Sn←N increase the coordination number of the central metal atom to six.

In one of the coordinated bismothol I ligand, the bond S(6)–C(1) 1.74 Å, S(7)–C(2) 1.752 Å are consistent with S–C 1.757 and 1.765 Å of SnPh$_2$Cl(tctsc) and SnCl$_2$(tctsc)$_2$ [18], 1.744 Å of [SnEt$_2$Cl.L] [19], which evidenced that the ligand coordinated as thiol but not thione isomers. The bond N(1)–N(2) 1.39 Å are very similar with N–N bond 1.390 Å in (t-Bu)$_2$Sn[Bis(1-phenyl-3-methyl-4-benzoyl–pyrazolon–5–ato)] [20], reflecting N–N exist as single bond, and the C(1)=N(1) 1.29 Å. C(2)=N(2) 1.33 Å are shorter than the double bond C=N 1.37 Å in (t-Bu)$_2$Sn[Bis(1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato)] [20], all of which indicates that bismothol I offered thiolate species to substitute the chloride atoms of dibutyltin dichloride. The coordination of other coordinated ligands in macrocyclic complex (I) are similar.

As shown in Figs. 1 and 2, complex (I) exists in a distorted octahedron geometry about all five tin atoms, where two sulfur atoms and two carbon atoms occupy the equatorial position and two azole-N atoms at axial position. The deviation from octahedron is indicated by the bond angles, N(1)–Sn(1)–N(10) 150.0°, N(2)–Sn(2)–N(3) 150.3°, N(4)–Sn(3)–N(5) 150.2°, N(6)–Sn(4)–N(7) 152.6°, N(8)–Sn(5)–N(9) 149.8° which deviate from the ideal angle 180°, respectively. Other tin atoms Sn(2), Sn(3), Sn(4) and Sn(5) have the same geometries as Sn(1).

3. Experimental details

3.1. Preparation of complex (I) $C_{50}H_{90}N_{10}S_{15}Sn_5$

The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. The 2,5-dimercapto-1,3,4-thiodiazole (0.30 g, 2 mmol) was added to the solution of ethanol 20 ml with sodium ethoxide (0.272 g, 4 mmol), and the mixture was stirred for 30 min, then add (n-Bu)$_2$SnCl$_2$ (0.607 g, 2 mmol) to the mixture, continuing the reaction for 12 h at 30 °C. After cooling down to room temperature, filtered it. The solvent of the filtrate was gradually removed by vaporation under vacuum until solid product was obtained. The solid was then recrystallized from ether-dichloromethane. Colourless crystal complex was formed. Yield, 72%. m.p.:248 °C(dec.). The C, H, N and S analyses were performed using a Perkin–Elmer PE-2400II CHNS Micro-analyser. Found: C, 31.48; H, 4.69; N, 7.38; S, 25.19. Calc. for $C_{50}H_{90}N_{10}S_{15}Sn_5$: C, 31.51; H, 4.76; N, 7.35; S, 25.24. IR(KBr, cm^{-1}): 2923 (m, C–H), 561 (m, Sn–C), 317 (m, Sn–S). ^{1}H-NMR (90 MHz, $CDCl_3$):δ 1.10–1.75 (m, $-CH_2CH_2CH_2$); 0.95(t, $-CH_3$).

3.2. *Crystal structure determination of complex (I) $C_{50}H_{90}N_{10}S_{15}Sn_5$*

Crystal data for $C_{50}H_{90}N_{10}S_{15}Sn_5$: crystal dimensions $0.20 \times 0.20 \times 0.10$ mm^3, $M = 1905.67$, monoclinic, space group $P2_1/c$, $a = 28.787(4)$, $b = 24.725(3)$, $c = 25.620(3)$ Å, $\beta = 115.490(2)°$, $V = 16460(4)$ Å^3, $Z = 8$, $\rho_{cak} = 1.538$ g cm^{-3}, λ(Mo–K$_\alpha$) = 0.71073Å, $\mu = 1.913$ mm^{-1}, $T =$ 298(2) K, 74631 reflections collected for $1.14 \leqslant 2\theta \leqslant 23.40°$, 23689 independent reflections. $R_1 = 0.0531$, $wR_2 = 0.1069$ for reflections with $I > 2\ \sigma(I)$. Data collection was by means of a Bruker SMART 1000 CCD diffractometer. The structure was solved by direct methods on F^2 using SHELXL-97 program. Largest difference peak and hole: 0.388 and −0.408 eÅ^{-3}.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambrige Crystallographic Data Center as supplementary publication no. CCDC-192509. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambrige, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.ck).

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