

Synthesis and Anion Recognition of a Novel Heterocyclic Organotin Complex

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Abstract: A novel heterocyclic hexacoordinate organotin(IV) complex, bis(*O*-vanillin)-semiethylenediamino dibenzyltin (VEDBT) was synthesized by the reaction of dibenzyltin dichloride with bis(*O*-vanillin)-semiethylenediamine, its structure has been characterized by spectral methods. The electrodes using VEDBT as a neutral carrier show high selectivity for salicylate anions.

Keywords: Heterocyclic organotin(IV) complex, synthesis, anion recognition, selectivity, salicylate.

Recently, there has been growing interest in organotin complexes, which demonstrate selective recognition for anions such as salicylate, phosphate, chloride, *etc*¹⁻³. The selectivities resulted from the unique interactions between the substrates and the anions, thus, this anion selectivity behavior is dependent on the properties of the central metal and the chemical environment around the central metal⁴. The Sn(IV) atom in these compounds is a typical Lewis acid and seems exhibit an unusual coordinate behavior with anions, a suitable charge density of the central Sn (IV) atom is very important for the unique interactions between the substrates and the analyzed anions⁵. In this work, bis(*O*-vanillin)-semiethylenediamino dibenzyltin(VEDBT), a novel heterocyclic hexacoordinate organotin () complex, was synthesized by the reaction of dibenzyltin dichloride with bis(*O*-vanillin)-semiethylenediamine, its structure has been characterized by spectral methods. The electrodes using VEDBT as a neutral carrier show high selectivity for salicylate anion.

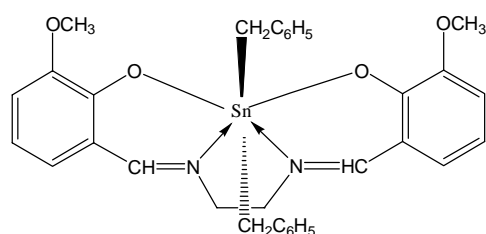
Synthesis of VEDBT

0.744 g (2 mmol) dibenzyltin dichloride⁶ was added to a mixture of 0.657 g (2 mmol) bis(*O*-vanillin)-semiethylenediamine and 0.172 g (4.4 mmol) sodium amide in 50 mL benzene. The reaction mixture was stirred for 4 h under refluxing, the resulted salts was removed by filtration, the filtrate was concentrated to give 0.598 g (47.58%) of brightly yellow crystal, m.p. 191-192.5°C. It can dissolve in chloroform, methanol, acetone and benzene. Anal, Calcd. for C₃₂H₃₂N₂O₄Sn: (%) C 61.27, H 5.14, N 4.47. Found: (%)C 61.38, H 5.05, N 4.52. The ESIMS indicated a molecular ion peak at *m/z* 627.2 (calcd. 627.3), other ion fragment peaks at 563(24), 464(23), 445(100), 267(23).

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In IR spectrum (KBr, cm^{-1}), 1629, 1393, 1201, 697, 563 can be assigned to C=N, C-N, Ph-O, Sn-O, Sn-C, respectively. Compared with the free ligand, the C=N stretching frequency shifted from 1633cm^{-1} to 1629cm^{-1} , the decrease in the C=N bond order due to the coordinate bond formation between the metal with the azomethine nitrogen atom⁷. The ^1H NMR spectrum (in CDCl_3 , see **Table 1**) showed that benzylic methylene protons signal at 2.963 ppm, which consists of a single peak and a pair of little satellite peaks, indicating Sn-H coupling. From its big coupling constant ($J_{\text{Sn-H}}=82$), we can deduce that VEDBT is a highly coordinated complex⁸. From above spectral data, the structure of VEDBT was deduced as **Figure 1**.

Figure 1 Structure of VEDBT



Anion recognition

A PVC membrane electrode incorporating VEDBT as neutral carrier was assembled according to Thomas and co-workers⁹⁻¹⁰. The membrane compositions were 3.5 wt% VEDBT, 66.5 wt% membrane solvent (didecyl phthalate) and 30.0 wt% PVC. The cell for millivolt measurements was as follows: Hg-Hg₂Cl₂ | KCl (satd.) | sample solution | membrane | 0.1 mol/L KCl | Hg-Hg₂Cl₂

The potentiometric response characteristics of the electrodes based on VEDBT are shown in **Figure 2**. The results indicated that these electrodes show a linear response to salicylate ranging from 1.0×10^{-1} to 7.59×10^{-5} mol/L with a slope of -66.37 mV/dec.

Anion selectivity coefficients, $\log K_{A,B}^{\text{Pot}}$, were determined by the separated solution method according to IUPAC recommendations¹¹ and were obtained with the respective 0.01 mol/L anion solutions of sodium salts in NaH_2PO_4 - Na_2HPO_4 buffer solution (pH 5.5). The single-ion activities were calculated by the extended Debye-Hückel equation. The results shown in **Table 2** indicate that these electrodes demonstrate excellent selectivity towards salicylate anions and exhibit a selectivity sequence of anions in the following order: salicylate > thiocyanate > perchlorate > iodide > nitrite > nitrate > chloride > bromide > sulfate. All these properties are interesting for their further applications.

Table 1 ^1H NMR data of VEDBT (in CDCl_3)

site	(ppm)	site	(ppm)
ethylene(-CH ₂ -CH ₂ -)	2.44(t, 4H)	phenenyl(C ₆ H ₅)	6.52-6.71(m, 6H)
methylene(-CH ₂ -Sn)	2.963(t, 4H)	Phenyl(C ₆ H ₅ -)	6.85-6.98(m, 10H)
methoxy (CH ₃ O-)	3.923(s, 6H)	methine(-N=CH-)	7.76(s, 2H)

Figure 2 Response characteristics of the membrane electrodes based on VEDBT towards salicylate

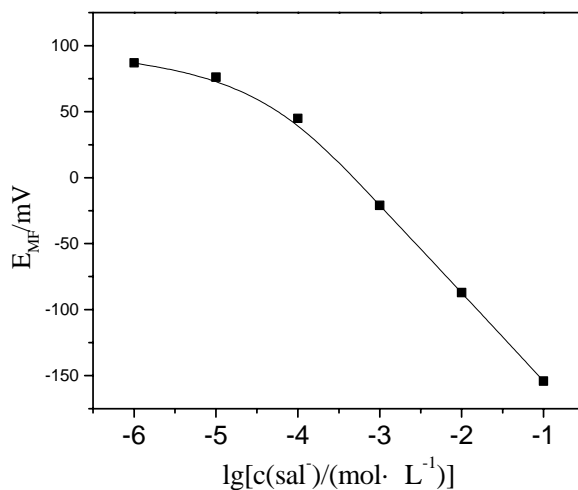


Table 2 Selectivity Coefficients, $\text{Log}K_{A,B}^{\text{Pot}}$

anion	salicylate	thiocyanate	perchlorate	iodide	nitrite	nitrate	chloride	bromide	sulfate
LogK	0	-1.05	-1.11	-2.18	-2.41	-2.56	-2.95	-2.95	-4.07

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