

Lanthanum complex for gas sensing

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The azomethine resulted from the reaction of 2,4-dihydroxybenzaldehyde with 1,3-bis(3-aminopropyl)tetramethyldisiloxane was used as a ligand for lanthanum complexation. The structure of the formed chelate was verified by spectral analyses. This complex, soluble in some common organic solvents, was tested as a sensing element in a gas sensor device for NO_x and CO₂ detection.

(Received October 20, 2008; accepted November 27, 2008)

Keywords: Gas sensor, Lanthanum complex, Azomethine, Thick and thin film technology

1. Introduction

The incorporation of the metals into an organic structure offers potential for the preparation of materials with properties that combines features of the two involved components. Coordination compounds constitute a very important field in chemistry because of their thermal stability, electrical conductivity and catalytic action, mainly in some of the chemical reactions occurring in biological materials [1]. Metal-ligand coordination provides an excellent pathway for the synthesis of supramolecular systems. This is due the fact that the coordination bond is highly directional, the ligand structures can be varied in a desired manner by well-known methods of the organic chemistry, and the thermodynamic and kinetic stability can be fine-tuned with the appropriate ligand types and metal ions [2].

Many studies are dedicated in the last time to synthesis of ligands based on the Schiff bases [3-5] due to their interesting properties such as thermal and mechanical resistance, environmental stability, semiconducting or optical properties and ability to form metal chelates having analytical and biological applications [6-8]. The properties of Schiff bases depend in great measure on the kind of amine and aldehyde from which they are obtained. The literature is scarce regarding siloxane azomethines synthesis. A series of polyazomethines containing pyridine ring and oligosiloxane moieties was synthesized as macromolecular tridentate ligands, and complexed with cobalt in order to obtain highly oxygen permselective membranes [9]. The synthesis and study of a series of siloxane-based azomethines was recently reported [10]. In this paper we report the use of such an azomethine to form a complex with a lanthanide, namely La. The lanthanides or their compounds are well known as being luminescent. As a result such compounds are largely used in optical devices. There has also been a growing interest in the development of lanthanide-doped polymers for numerous applications in fiber-optic communications systems, fiber

laser development, and optical sensing [11]. Present interest in lanthanide complexes is primarily motivated by applications in life sciences, mainly for developing chemical sensors or tools for medical diagnosis and therapy [12]. In this paper we tested the La complexed with siloxane-based azomethine in gas sensing.

2. Experimental

2.1. The preparation of the lanthanum complex

Materials

Lanthanum acetate, La(CH₃COO)₃ (Fluka AG), was used as received.

1,3-Bis(3-aminopropyl)tetramethyldisiloxane (Fluka AG), (AP₀), was used as received. 2,4-Dihydroxybenzaldehyde was prepared and purified according to procedure described in literature [13] (yield: 33%, m. p. 135-137° C).

The preparation of the bisphenol-azomethine, L

2,4-Dihydroxybenzaldehyde, AR, (0.50 g, 3.6 mmol) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane, AP₀, (0.5 ml, 1.8 mmol) were solved in 10 ml methanol under stirring and refluxed for 9 h. After partial solvent removing and cooling, the mixture was poured in a large excess of water when the bisphenol-azomethine (L) was separated by precipitation. The product was then washed with water, dried, weighted and analyzed.

The obtaining of complexed La, C

0.316 g (1 mmol) Lanthanum acetate dissolved in 10 ml water was gradually added to a solution containing 0.732 g (1.5 mmol) L solved in 10 ml methanol. The mixture was refluxed under stirring for 4h, and then was filtered. The filtrate was concentrated by partial solvent removing and precipitated in water. A yellow precipitate was laid down. The liquid was removed and the precipitate

was repeatedly washed with water and acetone and dried in vacuum at 40°C.

FT-IR absorption spectra were recorded with KBr pellets on a FT-IR Vertex 70 (Bruker, Germany).

¹H NMR spectra were taken on a JEOL C-60 HL spectrometer using TMS as internal standard.

2.2. The preparation of the sensor

The sensor was made by the thick film and thin film technologies. The substrate was an alumina plate 4x4x0.6 mm where the two plate electrodes were deposited by Ag ink using the screen-printed method with the electrode thickness of 35 μm and then heat-treated at 750°C for 1 hour. The complex C was dissolved in chloroform and coated as 200 nm thickness sensitive layer on the substrate by dip coating method. The dimensions of the sensitive layer were 3x3x0.6 mm. The sensor was mounted on the transistor ambasis with 12 pins. Fig. 1 shows the sensor configuration. The gases detection tests were performed in a NO_x and CO₂ atmospheres and the voltage measurements were performed with a multimeter APPA type.

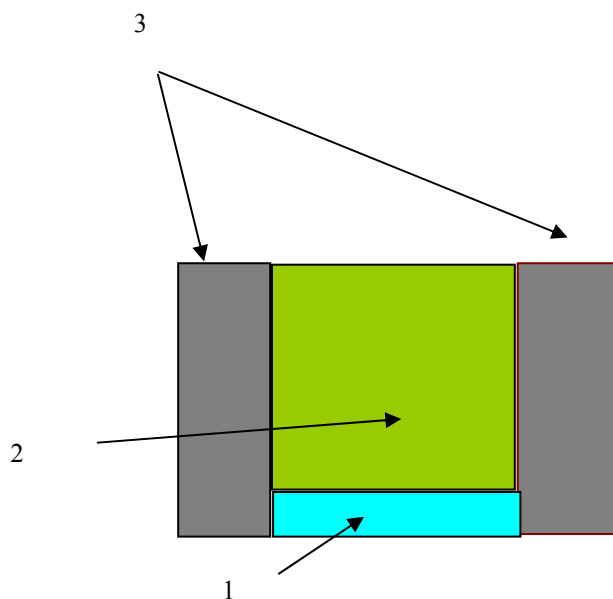
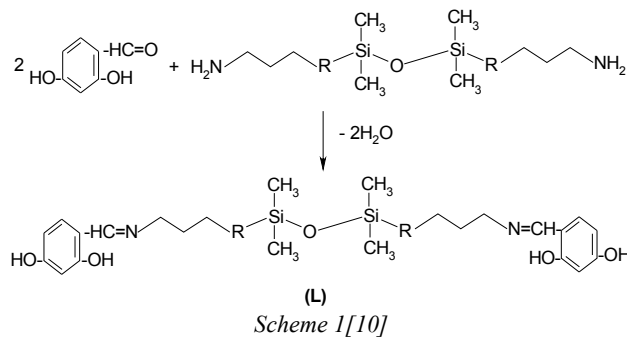


Fig. 1. The sensor configuration
1- alumina substrate; 2- sensitive layer; 3- electrodes.

3. Experimental results and discussion

The azomethine (L) was prepared by condensation of 2,4-dihydroxybenzaldehyde with 1,3-bis(3-aminopropyl)tetramethyldisiloxane in 2:1 molar ratio [10], according to Scheme 1:



The IR spectrum of the formed azomethine shows all the expected characteristic absorption bands (Fig. 2, L): 1643 cm⁻¹ (CH=N), 1610, 1542, and 1455 cm⁻¹ (phenyl vibrations), 1253 cm⁻¹ (Si-CH₃), 1042 cm⁻¹ (Si-O-Si).

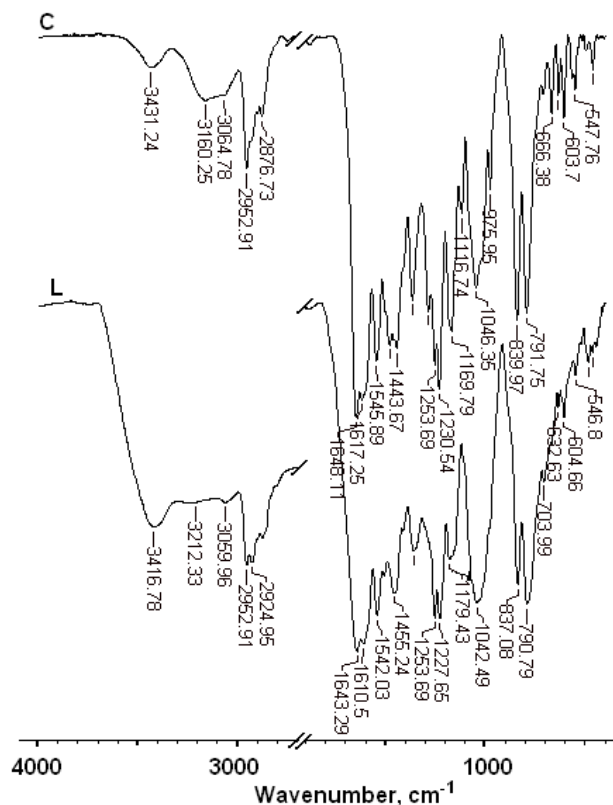


Fig. 2. The comparative FT-IR spectra of the azomethine ligand, L, and complexed La, C.

Significant modifications appear in the ¹H NMR spectrum of the azomethine as compared with that of the siloxane precursor, AP₀ (Fig. 3). So, chemical shifts corresponding to the protons from azomethine are: 8.3-8.2 ppm for CH=N-, 6.2-6.0 and 7.0-6.8 (aromatic CH), 3.6-3.1 (Si(CH₂)₂-CH₂-N=C) compared to 11.0-10.8 (CH=O), 6.5-6.3 and 7.6-7.4 (CH aromatic) in resorcylic aldehyde and 2.7-2.4 for (Si(CH₂)₂-CH₂-N=C) in 1,3-bis(3-aminopropyl)tetramethyldisiloxane [10].

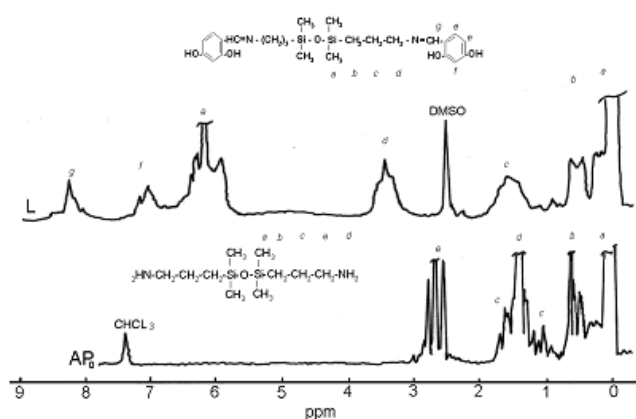
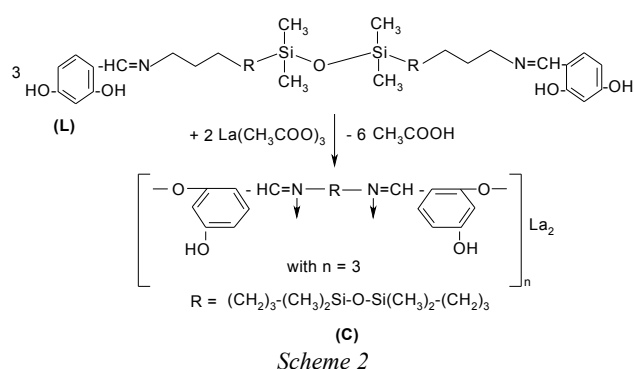


Fig. 3. ^1H MMR Spectrum of a polyazomethine of type L as compared with that of the starting diamine AP_0

The obtained siloxane-based azomethine ligand is soluble in a large range of solvents: CHCl_3 , acetone, THF, DMF, DMSO, MeOH.

The azomethines or Schiff bases polydentate ligands derived from hydroxybenzaldehyde are known to form stable complexes with transition metal ions [14]. Therefore, the synthesized bisphenol-azomethine having CN and OH groups in positions favorable for the closing of the chelate ring was used for complexing lanthanum. The lanthanides series (the first f -series) is closely related to that of the group 3 elements, and like these elements, the dominant oxidation state is always 3+. Their chemistry is predominantly that of ionic and weakly coordinated species analogous to the group 2 elements [15].

Thus, by treating bisphenol-azomethine ligand with lanthanum acetate, $\text{La}(\text{CH}_3\text{COO})_3$, a complex, C, of the type presented in Scheme 2 was obtained.



The formation of the complex was confirmed by IR spectrum (Fig. 2, C) where both band assigned to $\text{C}=\text{N}$ and those corresponding to the phenyl vibration are slight shifted to higher wave number (1648 and 1617, 1545, 1479 cm^{-1} , respectively) as a result of the lanthanum complexation. The bands assigned to $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{CH}_3$ can be seen at 1042 and 1253 cm^{-1} , respectively.

The metal presence is proved by the bands at 666 cm^{-1} ($\nu_{\text{Me}\rightarrow\text{O}}$) and 460 cm^{-1} ($\nu_{\text{Me}\rightarrow\text{N}}$) [16,17]. The medium

absorption bands in the region 3400-3000 cm^{-1} corresponding to phenolic $-\text{OH}$ stretching diminishes in the spectra of the chelate, indicating coordination.

The obtained complex dissolves with difficulty in a few solvents: methanol, acetone.

The complex was used as sensing element in the manufacturing a sensor device in order to test it in gas detection.

The sensor was exposed in 100 ppm NO_x and 1000 ppm CO_2 atmospheres. Fig. 4 shows the voltage-time characteristics. From the figure it can be seen that the lanthanum complex is more sensitive to NO_x when the developed maximum voltage signal was 78 mV while in the case of CO_2 it was only 12 mV in the condition of using a tenfold increased gas concentration. This behavior can be assigned to the powerful electron donor character of NO_x as compared with CO_2 . The nitrogen electrons are involved in the occupying of the free orbitals of the metal, thus improving the electrical properties of the material.

Another explanation would be the gas permselectivity of the sensitive layer conferred by the presence of the siloxane in the compound structure. That is more permeable for NO_x as compared with more polar and bigger CO_2 molecule. This is supported by the decrease of the voltage after the maximum is reached that can be due to the desorption process which is more rapid in the case of the NO_x .

In the both cases there is at least one intermediary step until the maximum voltage is reached. The diffusion process could be responsible for this.

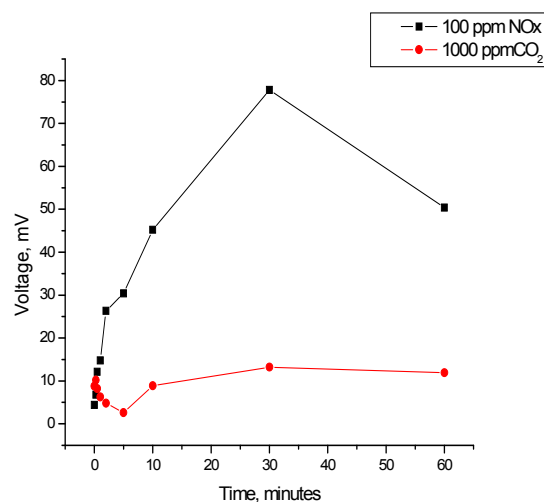


Fig. 4. The voltage-time characteristic for the lanthanum complex exposed to NO_x and CO_2

4. Conclusions

Lanthanum was complexed with a ligand prepared starting from 1,3-bis(3-aminopropyl)tetramethyldisiloxane and 2,4-dihydroxybenzaldehyde. The presence of the siloxane sequence in the complex confers certain solubility and, as a result, an improved processability. The film

obtained from chelate solution in chloroform was used as sensing element for manufacturing sensor. The device was tested in two different environments proving to be more sensitive at NO_x exposure as compared with CO₂.

Acknowledgements

This research occurred in the frame of Project CEEX-MATNANTECH 10/2005.

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