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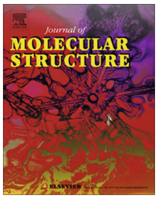

Holodirected coordination sphere around lead(II) in three-dimensional polymeric structure; New precursor for preparation of lead oxide sulfate nano-structures

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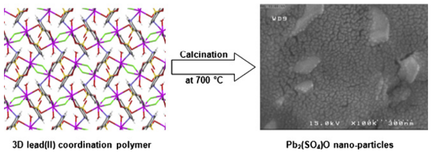
HIGHLIGHTS

- A new lead(II) three-dimensional polymer has been synthesized and characterized.
- The Pb ion has distorted octahedral coordination sphere with holodirected structure.
- Instead of PbO, $Pb_2(SO_4)O$ nano-particles was prepared from calcination of it.

GRAPHICAL ABSTRACT

A new lead(II) three-dimensional coordination polymer has been synthesized and characterized. The single-crystal X-ray data of compound **1** shows only one type of Pb^{II} ion with the coordination number of six, the lead atom has distorted octahedral coordination sphere containing stereo-chemically inactive lone pair. Instead of PbO, $Pb_2(SO_4)O$ nano-particles with regular morphology was prepared from calcination process of it.



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ABSTRACT

A new lead(II) three-dimensional coordination polymer, $[Pb_2(\mu_3\text{-ANS})_2(\mu_2\text{-Cl})_2(H_2O)_2]_n$ (**1**) [ANS^- = 4-amino-1-naphthalenesulfonate], has been synthesized and characterized. The single-crystal X-ray data of compound **1** shows only one type of Pb^{II} ion with coordination number of six, the lead atom has distorted octahedral coordination sphere containing stereo-chemically inactive electron lone pair. The thermal stability of **1** was studied by TG-DTA (Thermo gravimetric and differential thermal analyses). Regular morphology of $Pb_2(SO_4)O$ nano-particle was prepared from fine powders of compound **1** by calcination process at 700 °C. This nano-structure was characterized by XRD (X-ray powder diffraction) and SEM (Scanning electron microscopy).

Introduction

During the last two decades, supramolecular compounds have received great attention and the number of their synthesized compounds is still growing, which is mainly due to their potential application in various fields. A wide branch of supramolecular compounds which obtained from coordination bonds between metal centers and appropriate ligands is coordination polymer. The expression "coordination polymer" appeared early in the 1960s [1], therefore research in the area of coordination polymers has been taken for over fifty years, but design and construction of coordination polymers have grown very rapidly over the past decade [2–5]. In addition to coordination bonds, it is well-recognized

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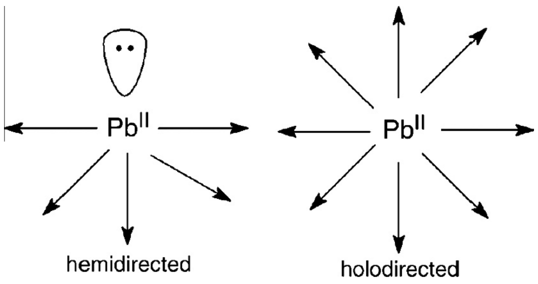
that weak inter atomic interactions, such as hydrogen bonding and π···π-stacking, have presented a synthetic paradigm for the rational design and synthesis of functional materials, in supramolecular chemistry [6]. Coordination polymers are a very important topic of modern solid state chemistry. Especially porous compounds have attracted a lot of attention due to their potentials as heterogeneous catalysts or adsorbents for gases like hydrogen and methane [7–10]. But besides porosity there are also attractive aspects of non-porous coordination polymers, e.g. magnetic, luminescent, vaporochromism or conducting properties to name a few [11–13]. Coordination polymers offer significant advantages over conventional molecular compounds due to very low solubility in conventional solvents and high thermal stability. They have also several applications in make sensors, organic light emitting diodes and full-colored LCD displays [14]. In contrast to coordination polymers of transition metal ions, the formation of polymers with heavy metal ions such as lead(II) is unreasonably sparse when compared with that of some other metals. Building new coordination polymers with Pb^{II} and modifying their structures is interesting in order to future study and support for this view. The coordination chemistry of lead(II) compounds are frequently discussed in regard to the coordination and stereo-activity of the valence shell electron lone pairs [15–20]. The lead coordination classify as holodirected which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of encompassing sphere and hemidirected which refers to those cases in which the bonds to ligand atoms are directed throughout only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand (Scheme 1). For divalent lead ions, relatively few structures are holodirected, especially with low coordination number [21]. Thus synthesis of metal coordination polymers is attracting interest in understanding how molecules can be organized and how functions can be achieved. The situation investigation of the stereo-chemical active valence shell electron lone pairs in the polymeric compounds may be more interested and the spontaneous aggregation of several bridging ligands may causes to disappearing of the gap and the coordination of lead(II) takes less common holodirected arrangement. Continuing to our previous works on Pb^{II} coordination polymers [20] and to extend the number of lead(II) coordination polymers with other organic ligands, in this work, we wish to report another lead(II) polymer from ANS^-. On the other hand, review of the related literature demonstrates that supramolecular polymers may be suitable precursors to the preparation of desirable nanoscale materials such as metal oxides with interesting advantages [22]. Thus in order to investigate the relation between the structure of initial precursors and the type of resulting nano materials, calcination of compound **1** was done at 700 °C in static atmosphere of air.



Scheme 1. Showing hemidirected and holodirected coordination sphere around Pb^{II} ion.

Experimental

Materials and physical techniques

All reagents for the synthesis and analysis were commercially available and used as received. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Nicolet 510P spectrophotometer. The thermal behavior was measured with a PL-STA 1500 apparatus between 22 and 900 °C in a static atmosphere of air. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromataed MoKα radiation. The structure was solved by direct methods and refined by full–matrix least–squares techniques on F^2. Structure solution and refinement was accomplished using SHELXL-97 program packages [23]. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using Mercury software [24]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromatized Cu Kα radiation. The samples were characterized with a scanning electron microscope with gold coating.

Synthesis of $[Pb_2(\mu_3\text{-ANS})_2(\mu_2\text{-Cl})_2(H_2O)_2]_n$ (1), preparations of its single crystals and $Pb_2(SO_4)O$ from this precursor

1 mmol (0.245 g) of 4-amino-1-naphthalenesulfonic acid sodium salt (Na^+ANS^-) was dissolved in 10 ml H_2O and was mixed and stirred with solution of 1 mmol (0.074 g) KCl in 3 ml H_2O, then a solution of 1 mmol (0.331 g) $Pb(NO_3)_2$ in 5 ml H_2O was added to the mixture and was refluxed for 3 h. After filtering it was allowed to evaporate for several days and then suitable light brown crystals were obtained. The crystals were washed with acetone and air dried, d.p. = 255 °C, Yield: 0.227 g (47%). IR (selected bands; in cm^{-1}): 425w, 511w, 555vs, 689vs, 812s, 821w, 943s, 999vs, 1035s, 1135vs, 1160vs, 1175vs, 1255s, 1444w, 1498s, 1600vs and 3010–3434 br. Anal. calc. for $C_{10}H_{10}ClNO_4PbS$: C, 24.87; H, 2.09; N, 2.90 %; found; C, 25.04; H, 2.14; N, 2.82 %. In order to preparation of $Pb_2(SO_4)O$ nano-structure, calcination of well scattered powder of compound **1** as a very thin film was done at 700 °C in a furnace and static atmosphere of air for 5 h.

Results and discussion

The reaction between 4-amino-1-naphthalenesulfonic acid sodium salt and $Pb(NO_3)_2$ provided a crystalline material of the general formula $[Pb_2(\mu_3\text{-ANS})_2(\mu_2\text{-Cl})_2(H_2O)_2]_n$ (**1**). The relatively weak absorption bands around 3000–3450 cm^{-1} in IR spectra is due to the C–H modes (involving the aromatic ring hydrogen atoms) and N–H modes (involving the $-NH_2$ group hydrogen atoms). The absorption bands with variable intensity in the frequency range 1444–1600 cm^{-1} correspond to vibrations of the phenyl rings. We expected that the characteristic band of the sulfonate group appears about 1345 cm^{-1}, but coordination of $-SO_3^-$ group to Pb^{II} ion, resulted in appearance of $-SO_3^-$ group at 1255 cm^{-1}.

Determination of the structure of **1** by X-ray crystallography (Tables 1 and 2), showed the complex to be a three-dimensional coordination polymer. Fig. 1a shows the primary dimmeric unit of compound **1**. As could be observed from this figure, ANS^- shows one type of coordination behavior and the sulfonate group of the ANS^- ligand acts as bidentate bridging group and two oxygen atoms of the sulfonate group coordinate to two Pb(II) ions. Thus another oxygen atom of sulfonate group does not coordinate to