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层状配位聚合物 $[Pb(NCS)_2(bpea)]_n$ 的合成, 结构和非线性光学性质(bpea = 1, 2- 双(4- 吡啶基)乙烷)

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室温下 $Pb(OAC)_2 \cdot 3H_2O$, KNCS, 和 1, 2- 双(4- 吡啶基)乙烷在甲醇中反应生成了八员环支撑的层状配位聚合物 $[Pb(NCS)_2(bpea)]_n$。三阶非线性 *Z*- 扫描研究表明该化合物具有非线性折射行为: 其非线性吸收系数 $\alpha_2 = 1.1 \times 10^{-11} m \cdot W^{-1}$, 非线性折射系数 $n_2 = 6.055 \times 10^{-18} m^2 \cdot W^{-1}$。

关键词: 配位聚合物 铅加和物 非线性光学性质 *Z*- 扫描

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Synthesis, Structure and Nonlinear Optical Properties of Layered Coordination Polymer $[Pb(NCS)_2(bpea)]_n$(bpea = 1, 2-bis(4-pyridyl)ethane)

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Under room temperature reaction of $Pb(OAc)_2 \cdot 3H_2O$ with KNCS, 1, 2-bis(4-pyridyl)ethane in CH_3OH afforded a novel layered coordinated polymer $[Pb(NCS)_2(bpea)]_n$ sustained by eight-numbered ring units. Investigation of third-order optical nonlinearity *Z*-Scan shows that it exhibit considerably nonlinear refractive properties with α_2 values of $1.1 \times 10^{-11} m \cdot W^{-1}$ and n_2 values of $6.055 \times 10^{-18} m^2 \cdot W^{-1}$ respectively.

Keywords: coordination polymer lead adduct nonlinear optical properties *Z*-scan

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0 Introduction

Early in the late 1960s Musgrave and coworkers synthesized the first complexes of the transition metals with 4, 4-bipyridine and suggested that these compounds are coordination polymers from the infrared spectra data[1]. Recent interest in the use of bipyridyl based bridging ligands and transition metal ions in the preparation of various layered architectures stems from the recognition that these polymeric frameworks possess potential useful properties such as catalysis[2], conductivity[3, 4], magnetism[5], and optical behavior[6] in material field. Although transition metal complexes are sufficient, only recently did lead complexes and adducts become the focus of many studies due to their structural diversity[7] and some polymeric species are also explored[8, 9]. It is still a challenge to prepare polymeric 4, 4′-bipyridyl dihalide or dithiocyanate adducts $[MX_2(4, 4'\text{-bipy})]_n$[10]. The number of these species is still small and those reported are mostly intractable powder precipitates which are insoluble in common organic solvents. Many structural information can only be extracted from power samples, which may strongly perturbed by a multi-phase. The adducts of MBr2 and MCl2 have been regarded as a layered architecture with semi-conductor properties[11] and hydrothermal synthesis has been proved by us and others to be an efficient approach for growing suitable sized crystals[5]. Comparably, The Pb-$(NCS)_2$ adducts [Pb (4, 4′-bipy) $(NCS)_2$] are relatively unexplored and the structure information on such compounds is still rather limited. It is known that no report on the crystal structure of this species has been published so far, but a few X-ray structures have been reported for the 2, 2′-bpy adducts[8]. Described here is the synthesis and characterizations of a new self-assembled coordination polymers $[Pb(bpea)(NCS)_2]_n$ [bpea = 1, 2-bis(4-pyridyl) ethane] and the non-linear optical properties for the compounds of this type are also studied.

1 Experimental

1.1 General

Solvents and the solid reagents were purchased as A. R. grade and used without further purification. Infrared spectra were recorded on a Fourier FT-10SX spectrophotometer with pressed KBr pellets. Carbon and hydrogen analyses were recordered on a PE 240C elemental analyzer. The compositions of lead were analyzed with a JA 1100 + 2000 ICP quantometer.

1.2 Synthesis of the Adduct

A solution of KNCS(19. 4mg, 0. 2mmol) and $Pb(OAc)\cdot 3H_2O$(37. 9mg, 0. 1mmol) in MeOH (4mL) was added to a solution of 1, 2-bis(4-pyridyl)ethane (18. 4mg, 0. 1mmol) in MeOH(5mL). The clear solution was left and the colorless crystals were obtained a week later. Yield: 0. 031g (62% based on Pb). It is stable in air and insoluble in common solvents and DMF. Anal. Calcd (found) for $C_{14}H_{12}PbS_2N_4$: C, 33. 12(33. 14); H, 2. 38(2. 37); N, 11. 04(10. 95). IR(KBr pellet, cm(1) 2010(vs, $\nu_{(NCS^-)}$), 1600(s), 1420(w); 1220(m), 1209(m), 1063(m), 1000(s), 825(s), 810(s), 750(w), 542(s), 530(s), 485(w), 470(w).

1.3 Crystallography

A colorless prismatic crystal was mounted on a glass fiber. All measurements were on a Simens Smart 1-K CCD area-detector diffractometer by using a ω-scan technique. The data reductions were

performed on a Silicon Graphics Indy workstation with Smart-CCD software. An empirical SADABS absorption correction was applied[12] . The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-PC (Version5. 1) package[13]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in their calculated positions (C-H 0. 96Å), assigned fixed isotropic thermal parameters(1. 2 times for CH_2 and 1. 5 times for CH_3 those of atoms to which they are attached) and allowed to ride on their respective parent atoms. Their contributions were included in the structure factor calculations.

1. 4 Optical Measurements

A DMF suspended solution of grinded sample was placed in a 5mm quartz cuvette for nonlinear optical (NLO) measurements. Their NLO properties were measured with an 8 ns pulse at 532nm generated from a Q-switched frequency-doubled Nd: YAG laser. The spatial profiles of the optical pulses were nearly Gaussian after passing through a filter. The pulsed laser was focused onto the sample cell with a 15 cm focal length mirror. The spot radius of the laser beam was measured to be 55μm. Incident and transmitted pulsed energies were measured simultaneously by two energy detectors(RJP-735 Energy probes, laser precision). The NLO properties of the sample were determined by performing Z-scan measurements. The sample was mounted on a translation stage that was controlled by the computer to move along the Z-axis with respected to the focal point. An aperture of 0. 5mm radius was placed in front of the transmission detector. The transmittance recorded as a function of the sample position on the Z-axis(closed-aperture Z-scan). For measuring the NLO absorptive, the Z-dependent sample transmittance was taken without the aperture(open-aperture Z-scan)

2 Results and Discussion

2. 1 IR

Thiocynate may be coordinated to metal atom in following three modes: N-bonding, S-bonding or bridging. The $\nu_{(NCS^-)}$ stretching frequency is generally observed in the range 2100 ~ 2050cm^{-1} for N-bonded thiocyanate, 2130 ~ 2085cm^{-1} for S-bonded thiocyanate and 2165 ~ 2065cm^{-1} for bridged thiocyanate groups[14, 15]. For the title compound the broad band attributable to the CN stretching mode is located at 2010cm^{-1}, which was found to be red-shifted relative to above three frequency ranges and indicated the presence of bridging mode.

2. 2 Crystal Packing

In the local structure of the title compound a distorted, octahedral coordination at each Pb is completed by a pair of axial nitrogen atoms of two bpea ligands, a pair of nitrogen atoms from two NCS groups and two neighboring S atoms through short contacts[16]; the latter four coordinated atoms constitute of the equatorial plane. The Pb-N distance is in agreement with strong Pb-N bonds with 2. 40 ~ 2. 71Å[8]. In ac plane polymeric 1-D linear chains are generated parallel to the c-axis, with adjacent chains staggered $a/2$ so as to provide a more efficient packing arrangement. In this structure, it is unexpectedly interesting that the terminal S atoms of the NCS^- ligands make short contacts with the Pb atom of a neighboring polymeric chain which is presumed to be an important

factor inducing the formation of the 2-D motif and stabilize the layer structure. For example, N(1)-Pb-N(2) is 81.0(4)° and two related $(NCS)_2$-connected Pb units form a pseudo-chair eight-numbered ring as shown in Fig. 1. The view from a-axis shows the crystal packing of these layered structures.

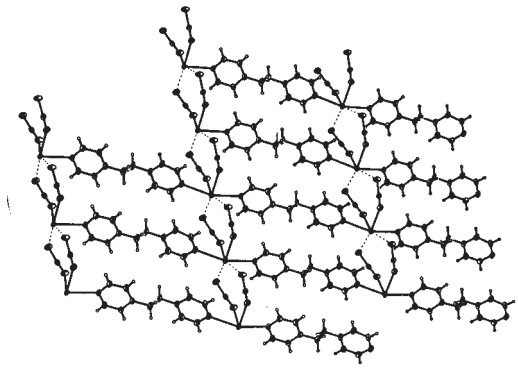

Fig. 1 View of a 2-D motif of $[Pb(NCS)_2bpea]_n$ in *ac* plane

2.3 Nonlinear Optical Properties

Fig. 2 shows typical *Z*-scan measurement of the compound in DMF suspended solution. Since light transmittance (T) is a function of the sample's *Z* position (with respect to the focal point at $Z = 0$). Nonlinear absorption ($\alpha = \alpha_2(I_i)$) and linear absorption (α_0) can be well described by equations (**1**) and (**2**):

Where α and α_0 are linear and effective third-order NLO absorptive coefficients. τ is the time, L is the optical path.

$$T(Z) = \frac{1}{\sqrt{\pi}\,q(Z)} \int_{-\infty}^{\infty} \ln[1 + q(Z)]\, e^{-\tau^2} d\tau \quad (1)$$

$$q(Z) = \alpha_2^{eff} I(Z) \frac{1 - e^{-\alpha_0 L}}{\alpha_0} \quad (2)$$

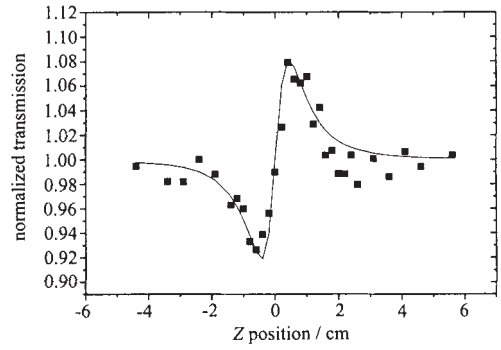

Fig. 2 Z-scan measurement of $[Pb(NCS)_2(bpea)]_n$ in a 1.4×10^{-4} mol · dm^{-3} DMF suspended solution

The nonlinear refractive component of the product was assessed by dividing the normalized *Z*-scan data obtained under open aperture configuration. An effective third-order nonlinear refractive index n_2 can be derived from the difference between normalized transmittance values at valley and peak positions ($\Delta T_{V\text{-}P}$) by using eqn. (**3**) with measured values $\Delta T_{V\text{-}P} = 1.231$ and 1.122:

$$n_2^{eff} = \frac{\lambda\alpha_0}{0.812\pi I(1 - e^{-\alpha_0 L})} \Delta T_{V\text{-}P} \quad (3)$$

The solid lines in Fig. 2 are the theoretical curves from eqn. (3). The effective α_2 values of 1.1×10^{-11} m · W^{-1} and n_2 value of 6.055×10^{-18} m^2 · W^{-1} for the sample, were derived from the theoretical curves respectively. The valley/peak pattern of the normalized transmittance curve obtained under closed aperture configuration shows characteristic self-focusing behavior of propagating light in the sample. This conclusion shows that polymeric species at suspended state possess special properties. Although many prudential work on second-order nonlinear optical effects of crystal or powder state coordination polymers have been studied[17~20], the related third-order NLO effects seem to remained unexplored, we hope the current work may present an useful reflection for this promising field. Further work on our research direction is in progress.

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