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Synthesis and characterization of a new metal-organic NLO material: Dibromo bis(triphenylphosphine oxide) mercury(II)

Li Li[a,b], Zhengping Wang[c], Xinyu Song[a], Sixiu Sun[a,*]

[a] Department of Chemistry, Shandong University, Jinan, Shandong 250100, PR China
[b] College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, Ningxia 750021, PR China
[c] State Key Lab of Crystal Materials, Shandong University, Jinan, Shandong 250100, PR China

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ABSTRACT

A new metal-organic nonlinear optical dibromo bis(triphenylphosphine oxide) mercury(II) ($HgBr_2(TPPO)_2$, TPPO = triphenylphosphine oxide) crystal has been synthesized. Single-crystal X-ray diffraction reveals that $HgBr_2(TPPO)_2$ crystallizes in the orthorhombic system, space group $Pna2_1$, $a = 21.174$ Å, $b = 9.1979$ Å, $c = 17.468$ Å, and $Z = 4$. The crystal was also characterized by FTIR spectroscopy, differential scanning calorimetry (DSC), thermal gravity analysis (TGA), and UV–vis–IR spectroscopy. Thermal analyses confirmed that the crystal is stable up to 151 °C. The transmission spectrum of the crystal shows that the lower cut off wavelength lies at 340 nm. The nonlinear optical (NLO) property of $HgBr_2(TPPO)_2$ has been estimated by Kurtz-powder second harmonic generation (SHG) test.

1. Introduction

In the last several decades, there has been considerable interest in the nonlinear optical (NLO) materials. In now days, NLO materials not only play an important part in solid state laser technique as frequency-conversion materials, but also have promising applications in the technology of information transmission, storage, extraction, processing and display [1–4]. Among various second order NLO materials, metal-organic coordination compounds have attracted much more attention due to their capability of combining the advantage of both organic and inorganic materials, such as high NLO coefficients, stable physico-chemical properties and better mechanical intension [5–7]. NLO material capable of frequency conversion is generally composed of an electron donor (D), an acceptor (A) and a conjugated π-system as a bridge providing the electronic communication between the donor and acceptor [8]. And for the second order NLO materials, the bridged system units must be packed in a non-centrosymmetric way. In metal-organic compounds, metal centers can act as both donors and the bridging moiety in D–π–A system, and the metal–ligand bond is expected to display large molecular hyperpolarizability because of the transfer of electron density between the metal atom and the conjugated ligand system [9]. The ferrocene derivative [10] is probably the best example. Furthermore, in the case of metal-organic coordination complex, the group IIB divalent d^{10} ions, Zn^{2+}, Cd^{2+}, and Hg^{2+} complexes have attracted our interest for their unique characteristics of pale color and high thermal stability. In this paper, we introduce the synthesis, characterization and NLO properties of a new metal-organic NLO crystal of $HgBr_2(TPPO)_2$.

2. Experimental

2.1. Material synthesis and crystal growth

All the starting materials were analytical reagent grade and used as purchased. $HgBr_2(TPPO)_2$ was synthesized by stoichiometric incorporation of $HgBr_2$ and TPPO. The calculated amount of salt was dissolved in absolute ethanol at room temperature. The solution was refluxed for 2 h, and precipitates were filtered off. The filtrate was then allowed to evaporate at room temperature. $HgBr_2(TPPO)_2$ salt was synthesized according to the reaction:

$$HgBr_2 + 2TPPO \rightarrow HgBr_2(TPPO)_2$$

The purity of the synthesized salt was improved by successfully recrystallization. Colorless and transparent single crystal of dimension 4 mm × 3 mm × 3 mm were obtained by slow evaporation technique from the saturated solution at room temperature. The crystal had good compositional stability and showed no degradation when stored in the open air for several months.

* Corresponding author. Tel.: +86 531 8836 4879; fax: +86 531 8856 446.
E-mail address: ssx@sdu.edu.cn (S. Sun).

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Table 1
Crystallographic parameters for $HgBr_2(TPPO)_2$.

Empirical formula	C_{36} H_{30} Br_2 O_2 P_2 Hg
Formula weight	916.95
Temperature	298
Crystal system	orthorhombic
Space group	$Pna2_1$
a (Å)	21.174(2)
b (Å)	9.1979(10)
c (Å)	17.468(2)
beta (°)	90.00
Volume (Å^3)	3402.1(7)
Z	4
Calculated density (mg m^{-3})	1.790
Absorption coefficient (mm^{-1})	6.998
F(0 0 0)	1768
Range of *h*, *k*, *l*	−27/23, −11/11, −22/13
Total reflections	19138
Independent reflections	2081
Papameters	388
R indices (*I* >2(*I*))	0.0261, 0.0470
R (all data)	0.0431, 0.0513
Goodness of fit on F^2	0.960

3. Characterization

Data collection were performed on a Bruker-Nonius SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K. The structure of the crystal was solved by direct method and refined by the full matrix-least-squares technique using the program SHELXL [11]. The FTIR spectrum was recorded in the 400–4000 cm^{-1} region, using KBr pellets on a Bruker vector-22 spectrometer. Differential scanning calorimetry and thermal gravity analysis (DSC/TGA) were carried out from room temperature to 600 °C by using a TA Instruments SDT Q600 under an N_2 atmosphere at a heating rate of 10 K min^{-1}. The transmission spectrum was recorded on a Hitachi U-4100 UV–vis–IR spectrophotometer, which can operate over the range 200–1200 nm at room temperature. The NLO property of $HgBr_2(TPPO)_2$ was tested by Kurtz powder SHG test using an Nd:YAG laser.

4. Results and discussion

4.1. Single crystal XRD

X-ray single crystal diffraction reveals that the grown crystal crystallizes in orthorhombic space group, $Pna2_1$ symmetry. The lattice parameters are *a* = 21.174 Å, *b* = 9.1979 Å, *c* = 17.468 Å, and *Z* = 4. A summary of the crystallographic data is given in Table 1. Selected bond distance and bond angle data are summarized in Table 2. The asymmetric unit is presented in Fig. 1. As depicted in Fig. 1, the central mercury atom was coordinated by two O atoms from TPPO ligand and two Br atoms. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 700822. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

Table 2
Selected bond distances and angles for $HgBr_2(TPPO)_2$.

Moiety	Distance (Å)	Moiety	Angle (°)
Hg1–O1	2.433 (3)	O1–Hg1–Br2	107.14 (8)
Hg1–O2	2.442 (3)	O1–Hg1–O2	90.49 (10)
Hg1–Br2	2.4406 (6)	Br2–Hg1–O2	102.11 (8)
Hg1–Br1	2.4491 (5)	O1–Hg1–Br1	93.47 (7)
O1–P1	1.487 (3)	Br2–Hg1–Br1	151.305 (19)
P2–O2	1.493 (4)	O2–Hg1–Br1	97.34 (8)
		P1–O1–Hg1	133.38 (19)
		P2–O2–Hg1	124.03 (18)

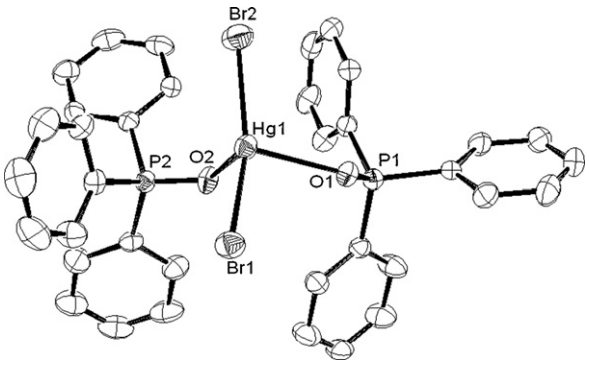

Fig. 1. The asymmetric unit of $HgBr_2(TPPO)_2$.

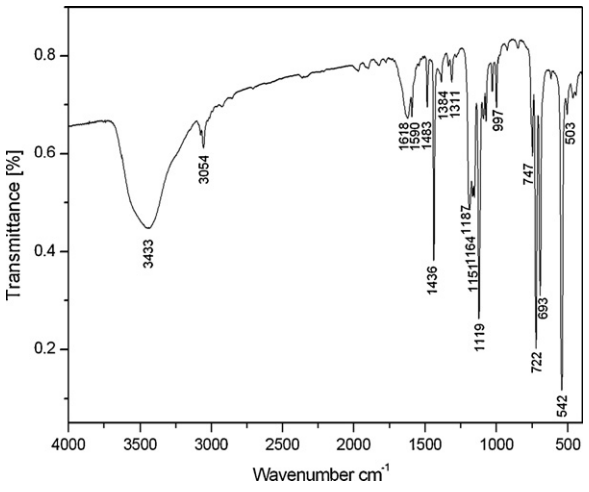

Fig. 2. FTIR spectrum of $HgBr_2(TPPO)_2$.

4.2. FTIR studies

The Fourier transform infrared (FTIR) spectrum of $HgBr_2(TPPO)_2$ is shown in Fig. 2 and compared with the standard spectrum of the TPPO ligand. The assignments along with TPPO are shown in Table 3. The stretching vibration of P=O (1190 cm^{-1}) shifts to lower frequency and splits into three sharp peaks (1187, 1164, and 1151 cm^{-1}), which clearly indicates the presence of oxygen to metal bonds in the coordination compound [12]. This is also confirmed by single crystal X-ray diffraction analysis. On coordination through oxygen, we can see from the FTIR spectrum, the nature of other vibration bands changes very slightly. The peak at 3433 cm^{-1} may be assigned for the stretching vibrations of the O–H bonds of water molecules absorbed by KBr.

Table 3
Comparison of the main FTIR spectral data of $HgBr_2(TPPO)_2$ with TPPO.

IR band (cm^{-1})		Assignment
TPPO	$HgBr_2(TPPO)_2$	
1190	1187, 1164, 1151	$\nu_{P=O}$
1439, 995	1436, 997	ν_{P-C}
1591, 1485	1588, 1484	$\nu_{C=C}$
3058	3054	ν_{C-H}

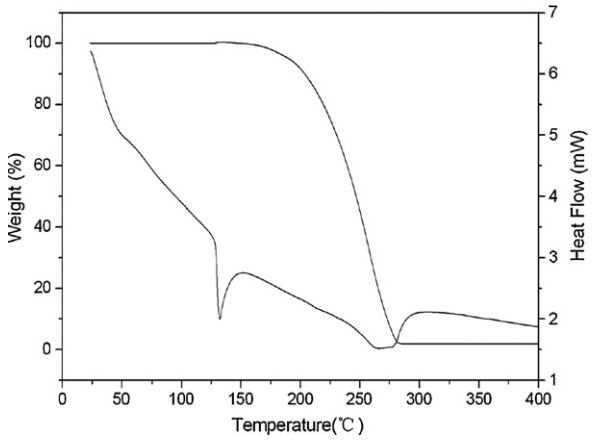

Fig. 3. DSC/TGA curves of $HgBr_2(TPPO)_2$.

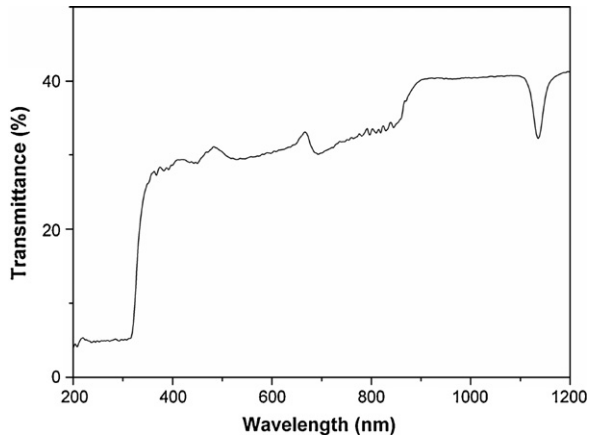

Fig. 4. Optical transmission spectrum of $HgBr_2(TPPO)_2$.

4.3. Thermal studies

TGA and DSC have been carried out for the grown crystals. TGA and DSC curves are shown in Fig. 3. $HgBr_2(TPPO)_2$ is thermally stable up to 151 °C. There is no phase transition till the material melts and this enhances the temperature range for the utility of the crystals for NLO applications. There is no detectable weigh loss below the decomposition temperature; therefore, the endothermic peak at 132 °C may correspond to the melting point of the grown crystal.

4.4. UV–vis studies

To find the transmission range of $HgBr_2(TPPO)_2$, we recorded the optical transmission spectrum of $HgBr_2(TPPO)_2$ between 200 and 1200 nm. The unpolished crystal with thickness of 3 mm was used. The transmittance spectrum was shown in Fig. 4. The cut-off wavelength of $HgBr_2(TPPO)_2$ occurs at 340 nm. The absence of the absorption at 1064 and 532 nm shows it could be used for optical window applications. The transparency of the crystal is low (30–40%), which can be improved by growing of higher optical quality single crystal.

4.5. Second harmonic generation

Kurtz powder technique [13] was used to estimate the relative second harmonic generation (SHG) activity of $HgBr_2(TPPO)_2$. A pulse energy of 4 mJ/pulse, pulse width of 10 ns, and repetition rate of 10 Hz are used. Powdered samples of standard KDP and compound $HgBr_2(TPPO)_2$ with the same particle size were considered for powder SHG measurements. It was found that the SHG efficiency of $HgBr_2(TPPO)_2$ is comparable with that of KDP. During the measurement, we also found that the crystal of $HgBr_2(TPPO)_2$ can reach phase matching. The SHG measurements on the crystal of $HgBr_2(TPPO)_2$ indicate the potential application of the material for frequency conversion process.

5. Conclusion

Single crystal of $HgBr_2(TPPO)_2$ was synthesized and grown from ethanol solution. The grown crystal was characterized by single-crystal XRD analysis. The study reveals that the crystal belongs to the orthorhombic system. The thermal behavior of the grown crystal was studied by using DSC/TGA. The Kurtz powder tests prove that the SHG efficiency of $HgBr_2(TPPO)_2$ is comparable with that of KDP. The SHG measurements on the crystal indicate that it is a potential candidate for NLO applications.

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