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A new screw shaped coordination compound for crystal engineering: Synthesis, crystal structure and nonlinear optical effect of *o*-chlorophenylthiourea zinc (II) diacetylacetonate

Xu Su^a, Gang Zhang^a, Tao Liu^a, Lianqing Chen^a, Jingui Qin^{a,*}, Chuangtian Chen^{b,*}

^a Department of Chemistry, Wuhan University, Wuhan 430072, China

^b Beijing Center for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Science, Beijing 100080, China

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Abstract

This paper presents the synthesis and crystal structure of a new screw shaped square–pyramidal coordination compound, $Zn(OCP-T)(acac)_2(OCPT is o-chlorophenylthiourea)$. In the molecule, the "tail" length is almost equal to the width of the "head". The compound crystallizes in a noncentrosymmetric structure. The molecules are arranged in almost parallel direction. The compound showed the powder SHG (second harmonic generation) effect of about 1.5 times as large as that of KDP. © 2006 Elsevier B.V. All rights reserved.

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Nonlinear optical (NLO) materials have played important role in the opto-electronic technology [1,2]. To show NLO effect, the crystal or film must form noncentrosymmetric (NCS) arrangement of the molecules that also possess no centrosymmetry [3]. Organic NLO chromophores are normally linear molecules with D– π –A character (D: electron donor, A: electron acceptor, π : conjugated bridge). This type of molecules exhibit quite large dipole moment, and interact each other by Coulombic force. In most cases, this interaction leads to the centrosymmetrical arrangement of the molecules, and hence no second harmonic generation (SHG) effect could be observed.

It has been called "Crystal Engineering" of NLO materials to form NCS arrangement of the chromophores in crystals or other types of the solids. This is one of the great challenges in the area though there have been some approaches to increase the chance for formation of NCS arrangement, such as the usage of the hydrogen bonding, chiral molecule, LB film and poled polymer among the others. It was recently reported that the polar chromophores could arrange favorably to form NCS packing in poled polymer films if bulky groups are attached to one or both sides of the chromophore molecules since the distance between the neighboring polar molecules are enlarged and the Coulombic interaction of the polar chromophores will be suppressed [4,5].

We have summarized in a review article [6] that square-pyramidal coordination compounds, $L \cdot Zn(acac)_2$, have a high probability to form NCS crystals. For example, phenylthiourea zinc (II) diacetylacetonate (PZDA) (see Fig. 1a) crystallized in an almost parallel arrangement of the molecules and showed SHG effect 10 times as large as that of KDP [7]. Later Anthony and Radhakrishnan have further called $L \cdot Zn(acac)_2$ as the screw shaped molecules, and presented one of the compounds, Zn(dimethylpyridene)(acac)_2,formed perfect assembly by selfpoling [8]. Three years ago,four compounds of the type of $L \cdot Zn(acac)_2$ with extended conjugation length of L were synthesized in the hope to increase NLO property (see Fig. 1b). However all four compounds crystallize in

^{*} Corresponding authors. Tel./fax: +86 27 68756757. *E-mail address:* jgqin@whu.edu.cn (J. Qin).



Fig. 1. (a) The molecule of PZDA; (b) the coordination compounds with long ligands.

centrosymmetric space groups, and showed no SHG effect [9,10]. It seemed to us that the screw shape of the molecule can not guarantee the formation of NCS, and it may be necessary to consider the ratio of the length to the width in the "screw". In our case, the compounds in Refs. [8,9] may be a little too long, and the ratio is a little too high. Therefore we have recently synthesized some new $L \cdot Zn(acac)_2$ with a shorter L. This paper describes the synthesis, crystal structure and NLO property of one compound, namely (*o*-chlorophenylthiourea zinc(II) diacetylacetonate.

The synthetic route is illustrated in Scheme 1. The ligand *o*-chlorophenylthiourea was synthesized by an operation described in Ref. [11]. The acetone zinc (II) diacetylaceto-nate (acetone–ZDA) was prepared according to the literature [12]. The coordination compound was prepared by reaction of (2-chloro-phenyl)-thiourea with acetone solution of equimolar acetone–ZDA at 45 °C for about 5 h. The product was purified by recrystallization from a mixture of acetone and acetylacetone (2:1 volume ratio). The ligand and the coordination compound were characterized by IR and EA.¹

Single crystals of the coordination compound were grown from an acetone–acetylacetone (1:1) solution by solvent evaporation in air and the structure was determined by X-ray single crystal structure analysis.² The ORTEP drawing of the compound with numbered atoms







Fig. 2. ORTEP view of the molecular structure of coordination compound. Selected Bond lengths (Å) and Angels (°): Zn(1)-O(1) 2.011(11), Zn(1)-O(2) 2.054(9), Zn(1)-O(3) 2.063(10), Zn(1)-O(4) 2.011(9), Zn(1)-S(1) 2.380(4), C(7)-N(2) 1.274(19), C(7)-N(1) 1.329(18), C(7)-S(1) 1.704(13), C(9)-O(1) 1.219(19), C(11)-O(2) 1.243(17), C(14)-O(3) 1.238(16), C(16)-O(4), 1.295(17), C(6)-Cl(1) 1.696(17), C(5)-N(1) 1.43(2); O(4)-Zn(1)-O(1) 144.0(5), O(4)-Zn(1)-O(2) 83.4(4), O(1)-Zn(1)-O(2) 87.7(5), O(4)-Zn(1)-O(3) 88.9(4), O(1)-Zn(1)-O(3) 85.7(4), O(2)-Zn(1)-O(3) 156.9(5), O(4)-Zn(1)-S(1) 109.3(3), O(1)-Zn(1)-S(1) 106.6(4), O(2)-Zn(1)-S(1) 100.7(4), O(3)-Zn(1)-S(1) 102.4(3).

is shown in Fig. 2. The zinc atom is coordinated to four oxygen atoms of two (acac) groups and one sulfur atom of ligand to form a square–pyramid configuration. The whole molecule can be seen as a screw, in which two (acac) groups form the "head" and the ligand forms the "tail". The ratio of the tail length to the head width is nearly 1:1. Four Zn–O bond lengths are not equal but have a disparity of about 0.05 Å at maximum. The

¹ Ligand: Yield 72%. IR data (KBr, cm⁻¹): 3415.2, 3187.6, 3270.5, 3066.4, 1618.8, 1579.5, 1501.1, 1453.2, 1481.4, 1233.4, 1057.4, 804.5, 614.2. Anal. (%), Found: C: 44.90, H: 3.92, N: 15.22, S: 17.01; (Calcd.: C: 45.04, H: 3.78, N: 15.01, S: 17.18). Coordination compound: Yield 59%. IR data (KBr, cm⁻¹): 3392.0, 3165.2, 3265.2, 3032.2, 2954.6, 2916.0, 1633.9, 1591.7, 1521.5, 1494.0, 1454.9, 1264.8, 1186.5, 1015.7, 800.5, 761.1. Anal.(%), Found: C: 45.44, H: 4.58, N: 6.20, S: 7.22; (Calcd.: C: 45.26, H: 4.70, N: 6.22, S: 7.12).

² Crystal data for compound: C₁₇H₂₀ClN₂O₄SZn, M = 449.23, monoclinic, space group Pc, a = 7.534(3) Å, b = 14.314(5) Å, c = 9.316(3) Å, $\beta = 95.113(6)^{\circ}$, V = 1000.6(6) Å³, T = 292(2) K, Z = 2, $D_c = 1.491$ g/cm³, $\mu = 1.489$ mm⁻¹, F(000) = 462, $\lambda = 0.71073$ Å. Of 2301 reflections measured, 1625 were unique ($R_{\rm int} = 0.0181$) and were used in all calculations. The final $R_1[I > 2\sigma(I)] = 0.0701$, $wR_2 = 0.1814$ (all data). The CCDC #: 605779.



Fig. 3. The crystal packing along *a* direction.

C(7)—S bond length is 1.704(13) Å, which is between 1.82 Å for C—S single bond and 1.56 Å for C=S double bond [11].

Fig. 3 is the crystal structure along *a* axis. All the screw shaped molecules orient in such an almost perfect direction that they parallel to each other along the *c* axis (with an angle of about 30° between two tails). The screw tails are located between every two screw's heads. This molecular alignment benefits the accumulation of the first molecular hyperpolarizability (β) and hence to exhibit a noticeable SHG value.

The SHG effect was investigated using the Kurtz powder technique [13]. A Nd:YAG laser with pulse duration of 8 ns was utilized to generate fundamental 1064 nm light. The microcrystalline potassium dihydrogen phosphate (KDP) was served as the standard. The result showed that the intensity of the frequency signal of the compound was about 1.5 times as large as that of KDP. No SHG signal was found for the ligand. The UV–Vis absorption maxima of the ligand and the coordination compound are at 295 and 321 nm, respectively. They both do not absorb at 532 nm.

In summary, a new screw shaped square–pyramidal coordination compound, $Zn(OCPT)(acac)_2$, in which the tail length is almost equal to the width of the head,was synthesized. In the crystal the molecules are arranged in almost parallel direction. And the powder SHG effect of the compound is about $1.5 \times KDP$. This result may indicate that the screw shaped dipole molecules should possess adequate ratio of the tail length to the head width so that they have more chance to form noncentrosymmetric and favorable alignment of the chromophores in crystals for NLO effect.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2006.05.034.

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