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Hydrothermal synthesis, crystal structure and third-order non-linear optical property of a copper chloride cluster

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A novel one-dimensional chain coordination polymer $[[\text{CuCl}_2]_2(\text{phen})_2]_\infty$ (**1**) and a three-dimensional coordination polymer $[[\text{CuCl}](\text{phen})_2](\text{CuCl}_2)$ (**2**) were synthesized from simple hydrothermal reactions and the structures were characterized with elemental analysis, FT-IR spectrum and X-ray diffraction. Compound **1** crystallized in the monoclinic space group Cc with $a = 9.874(2)$, $b = 17.871(4)$, and $c = 13.440(3)$ Å, $\alpha = 90.00^\circ$, $\beta = 106.59(3)^\circ$, $\gamma = 90.00^\circ$, $R_1 = 0.0463$, $wR_2 = 0.0819$. Compound **2** crystallized in the monoclinic space group $P2/c$ with $a = 14.4084(13)$, $b = 12.6280(11)$ and $c = 13.3560(12)$ Å, $\alpha = 90.00^\circ$, $\beta = 111.490(2)^\circ$, $\gamma = 90.00^\circ$, $R_1 = 0.0771$, $wR_2 = 0.1439$. In the packing structure, π - π stacking interactions are the most significant factors controlling the novel supramolecular sheets for the title compound. Moreover, the third-order non-linear optical property of the two compounds were also investigated and they show reverse saturable absorption and self-focusing performance.

Keywords: Organic–inorganic hybrid; 1,10-Phenanthroline; Copper halide cluster; Crystal structure; Hydrothermal synthesis; Third-order non-linear optical property

1. Introduction

Organic–inorganic coordination polymers have received extensive attention in recent years owing to their great fundamental and practical interest, especially hybrid copper halides. The architectures of copper halides can be tuned at the molecular level to give unusual electronic properties, various components and potential applications in areas of molecular adsorption, catalysis, electromagnetism, and photochemistry [1–21]. It is therefore vital to design and synthesize novel organic–inorganic hybrid copper halides to explore their various properties. A recent advance in this

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system is to design the coordination frameworks of copper halides by the incorporation of various organic structure-directing agents. More recently, owing to the introduction of the hydrothermal technique and various N-containing organic templating agents, a variety of novel organic–inorganic hybrid copper halides have been isolated with one-dimensional (1D) chain-like [5, 6] and two-dimensional (2D) layer-like structures [3, 9]. To date, the basic copper halide skeletons of these complexes exhibit several geometrical motifs: cyclic Cu_2X_2 dimeric [9], cubane tetrameric [12], zigzag polymeric [12], and “stair step” oligomeric [9] structures. The introduction of new organic templating agents leads to dramatic structural change of the basic inorganic phases [3], which have been exemplified by the reports of the Zubietta [3, 4, 8] and Willett groups [2, 14, 15]. Herein, two novel structures of compounds obtained under fairly mild hydrothermal conditions are presented, both reveal third-order non-linear optical (NLO) property.

2. Experimental

2.1. General procedures

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Copper was determined by a Leaman inductively coupled plasma (ICP) spectrometer. Electron spin resonance (ESR) spectra were recorded on a Japanese JES-FE3AX spectrometer at 298 K. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$.

2.2. Hydrothermal synthesis

2.2.1. Compound 1. A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, *o*-phen, and H_2O with the molar ratio of 1:1.6:445 was stirred for 20 min, sealed in a 15 mL polyfluoroethylene-lined stainless steel bomb, and kept at 160°C under autogenous pressure for 3 days. After cooling to room temperature, yellow chunk crystals of **1** were isolated in ca 50% yield (based on Cu) by mechanical separation from a green amorphous solid. The crystals of **1** were washed several times with distilled water and dried in air. The pH of the solution changed from 6 to 1, which indicated that HCl was produced during the hydrothermal reaction process. Elemental analysis found: C, 37.94; H, 2.12; Cu, 33.52; N, 7.36%; Calcd for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{Cu}_2\text{N}_2$ (**1**): C, 37.99; H, 2.11; Cu, 33.77; N, 7.39%.

Compound $[[\text{CuCl}](\text{phen})_2](\text{CuCl}_2)$ (**2**): the same conditions were used as for compound **1**, but kept at 160°C under autogenous pressure for 7 days. Elemental analysis found: C, 30.18; H, 2.26; Cu, 13.46; N, 5.78%; Calcd for compound **2**: C, 30.25; H, 2.52; Cu, 13.45; N, 5.88%.

2.3. X-ray crystallography

The structures of both compounds were determined by single-crystal X-ray diffraction. Data were collected on an *R*-axis RAPID IP diffractometer. An empirical absorption

Table 1. Crystal data and refinement summary for complexes

Complexes	1	2
Empirical formula	C ₂₄ H ₁₆ Cl ₄ Cu ₂ N ₄	C ₁₂ H ₁₂ ClCuN ₁₂ O ₁₂
Formula weight	629.29	615.33
Temperature	293(2) K	293(2) K
Crystal system, space group	Monoclinic, <i>Cc</i>	Monoclinic, <i>P2/c</i>
Unit cell dimensions	<i>a</i> = 9.874(2) Å <i>b</i> = 17.871(4) Å <i>c</i> = 13.440(3) Å $\alpha = 90^\circ$ $\beta = 106.59(3)^\circ$ $\gamma = 90^\circ$	<i>a</i> = 14.4084(13) Å <i>b</i> = 12.6280(11) Å <i>c</i> = 13.3560(12) Å $\alpha = 90^\circ$ $\beta = 111.490(2)^\circ$ $\gamma = 90^\circ$
Volume	2272.9(8) Å ³	2261.2(3) Å ³
Z, Calculated density	4, 1.839 Mg m ⁻³	3, 1.356 Mg m ⁻³
Crystal size	0.358 × 0.336 × 0.228 mm ³	0.356 × 0.338 × 0.226 mm ³
<i>F</i> (000)	1256	930
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0463, <i>wR</i> ₂ = 0.0819	<i>R</i> ₁ = 0.0771, <i>wR</i> ₂ = 0.1439
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0705, <i>wR</i> ₂ = 0.0844	<i>R</i> ₁ = 0.1812, <i>wR</i> ₂ = 0.2032

Table 2. Bond lengths(Å) and angles(deg) for complexes.

	1		2
Cu(1)–N(4)	2.052(6)	Cu(1)–N(3)	2.000(9)
Cu(1)–N(3)	2.045(7)	Cu(1)–N(2)	2.001(8)
Cu(1)–Cl(2)	2.256(2)	Cu(1)–N(1)	2.123(9)
Cu(1)–Cl(1)	2.261(2)	Cu(1)–N(4)	2.131(8)
Cu(1)–Cl(3)	2.711(3)	Cu(1)–Cl(4)	2.290(3)
Cu(2)–N(1)	2.029(6)	Cu(2)–Cl(1)	2.088(3)
Cu(2)–N(2)	2.054(6)	Cu(2)–Cl(1)	2.088(3)
Cu(2)–Cl(4)	2.251(2)	Cu(3)–Cl(3)	2.066(4)
Cu(2)–Cl(3)	2.289(2)	Cu(3)–Cl(3)	2.066(4)
N(2)–C(10)	1.293(9)	N(4)–C(24)	1.322(13)
N(2)–C(11)	1.341(9)	C(2)–C(1)	1.396(17)
N(4)–Cu(1)–N(3)	81.1(2)	N(3)–Cu(1)–N(2)	169.0(3)
N(4)–Cu(1)–Cl(2)	163.4(2)	N(3)–Cu(1)–N(1)	94.1(4)
N(3)–Cu(1)–Cl(2)	91.63(19)	N(2)–Cu(1)–N(1)	80.1(3)
N(4)–Cu(1)–Cl(1)	92.00(18)	N(3)–Cu(1)–N(4)	80.2(4)
N(3)–Cu(1)–Cl(1)	171.4(2)	N(2)–Cu(1)–N(4)	94.7(3)
Cl(2)–Cu(1)–Cl(1)	93.64(9)	N(1)–Cu(1)–N(4)	121.2(3)
N(4)–Cu(1)–Cl(3)	92.61(19)	N(3)–Cu(1)–Cl(4)	94.9(3)
N(3)–Cu(1)–Cl(3)	92.7(2)	N(2)–Cu(1)–Cl(4)	96.0(2)
Cl(2)–Cu(1)–Cl(3)	102.65(9)	N(1)–Cu(1)–Cl(4)	124.9(3)
Cl(1)–Cu(1)–Cl(3)	92.85(9)	N(4)–Cu(1)–Cl(4)	114.0(2)

correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97 software [16]. All of the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps. Structure solution and refinement with $I > 2\sigma(I)$ gave $R_1 = 0.0463$, $wR_2 = 0.0819$, $\{R_1 = \Sigma \|F_o\| - |F_c| / \Sigma \|F_o\|$; $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}\}$. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. Description of the structure

The single crystal X-ray diffraction analysis reveals that the structure of **1** consists of copper(II) chloride 1D chains with half-coordinate Cu–Cl bonds; the two-nucleus unit is bridged directly on the Cu(II) sites of the skeleton. There are two crystallographically unique Cu atoms in the asymmetrical structural unit, as shown in figure 1(a). The Cu(1) site is six-coordinate with two N donors provided by the chelating *o*-phen ligand, one μ_2 -Cl and end-Cl donors. The average distance of Cu(1)–N bonds is 2.052 Å, while Cu(1)–Cl bonds are in the range 2.256(2)–2.711(3) Å. The angles of the Cu(1) site vary from 81.1(2) to 171.4(2)°. The Cu(2) site is five-coordinate with three μ_2 -Cl donors. The Cu(2)–Cl average distance is 2.2270 Å and the Cl–Cu(2)–Cl angles are 93.91(9)°. To our knowledge, such basic skeleton unit combined with *o*-phen groups has never been reported. The basic Cu–Cl building blocks of **1** form an infinite 1D chain (figure 1b and tables 1 and 2).

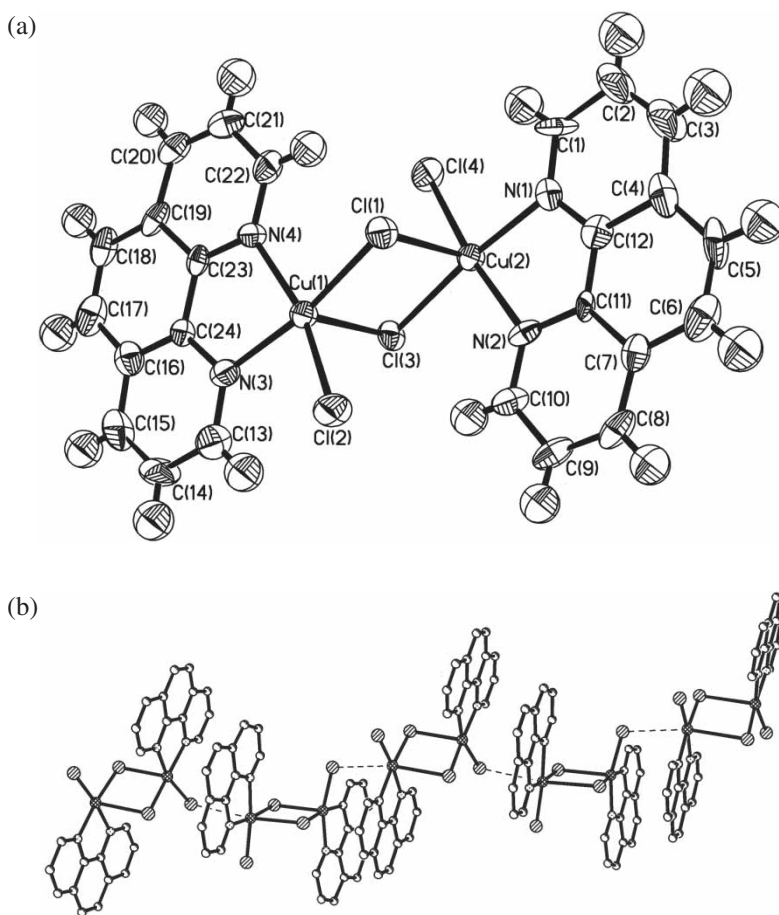


Figure 1. (a) ORTEP drawing of the unsymmetrical structural unit of **1** (50% probability ellipsoids) and the atom labeling scheme. (b) View of the 1D chain structure of **1** extending along the *a* axis.

The single crystal X-ray diffraction analysis reveals that in the structure of **2** *o*-phen plays a double role, as shown in figure 2(a). One acts as a covalently linked ligand. The adjacent phen rings are parallel to each other and cause significant π - π stacking interactions which lead to the generation of three-dimensional (3D) supermolecular architecture [22, 23]. The Cu(1) site exhibits five-coordinate geometry with four

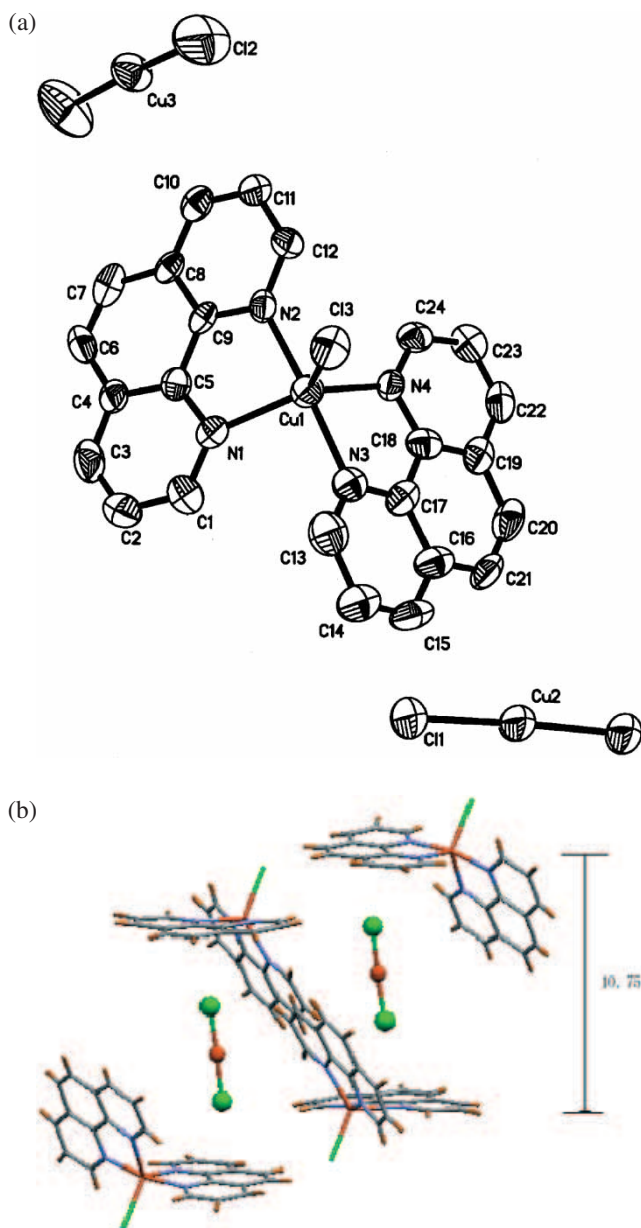


Figure 2. (a) ORTEP drawing of the unsymmetrical structural unit of **2**. (b) View of the 2D stacking arrangement of **2** along *a* axis. (c) View of the 3D stacking arrangement of **2**.

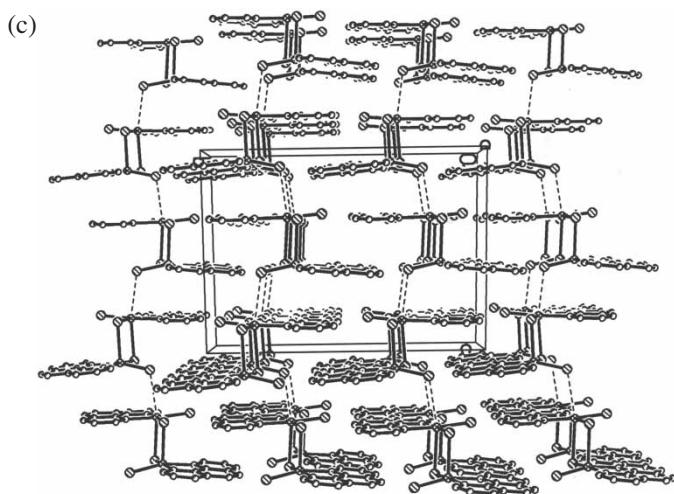
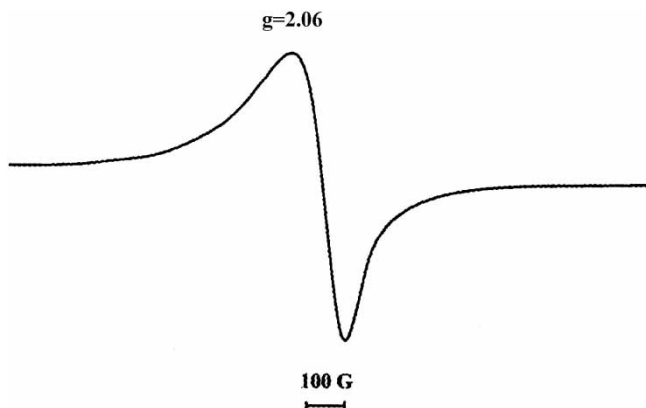


Figure 2. Continued.

Figure 3. The ESR spectrum of **1**.

N donors provided by the chelating *o*-phen ligands, and one Cl donor. The Cu(1)–N distance are in the range 2.000(9)–2.131(8) Å, Cu(1)–Cl(4) bond is 2.290(3) Å. The angles of the Cu(1) site vary from 80.1(3) to 169.0(3)°. The Cu(2) site is two coordinate with two Cl donors. The Cu(2)–Cl average distance is 2.088(3) Å and the Cl–Cu(2)–Cl angles are 177.1(2)°. The Cu(3)–Cl average distance is 2.066(4) Å and the Cl–Cu(3)–Cl angles are 176.2(3)°.

The π – π stacking interactions among benzene rings are also important to the structure. Benzene rings of the adjacent layers are trans-parallel to each other to form π – π stacking interactions, characterized by the contact distance of 10.75 Å, as shown in figure 2(b). The title compound is constructed into 3D supramolecular networks via the secondary bonding interactions as shown figure 2(c).

The FT-IR spectrum of complex **1** shows: 1625(w), 1607(w), 1585(w), 1514(m), 1493(w) cm^{-1} attributed to C=C or C=N stretching vibration, 856(s), 720(s) cm^{-1}

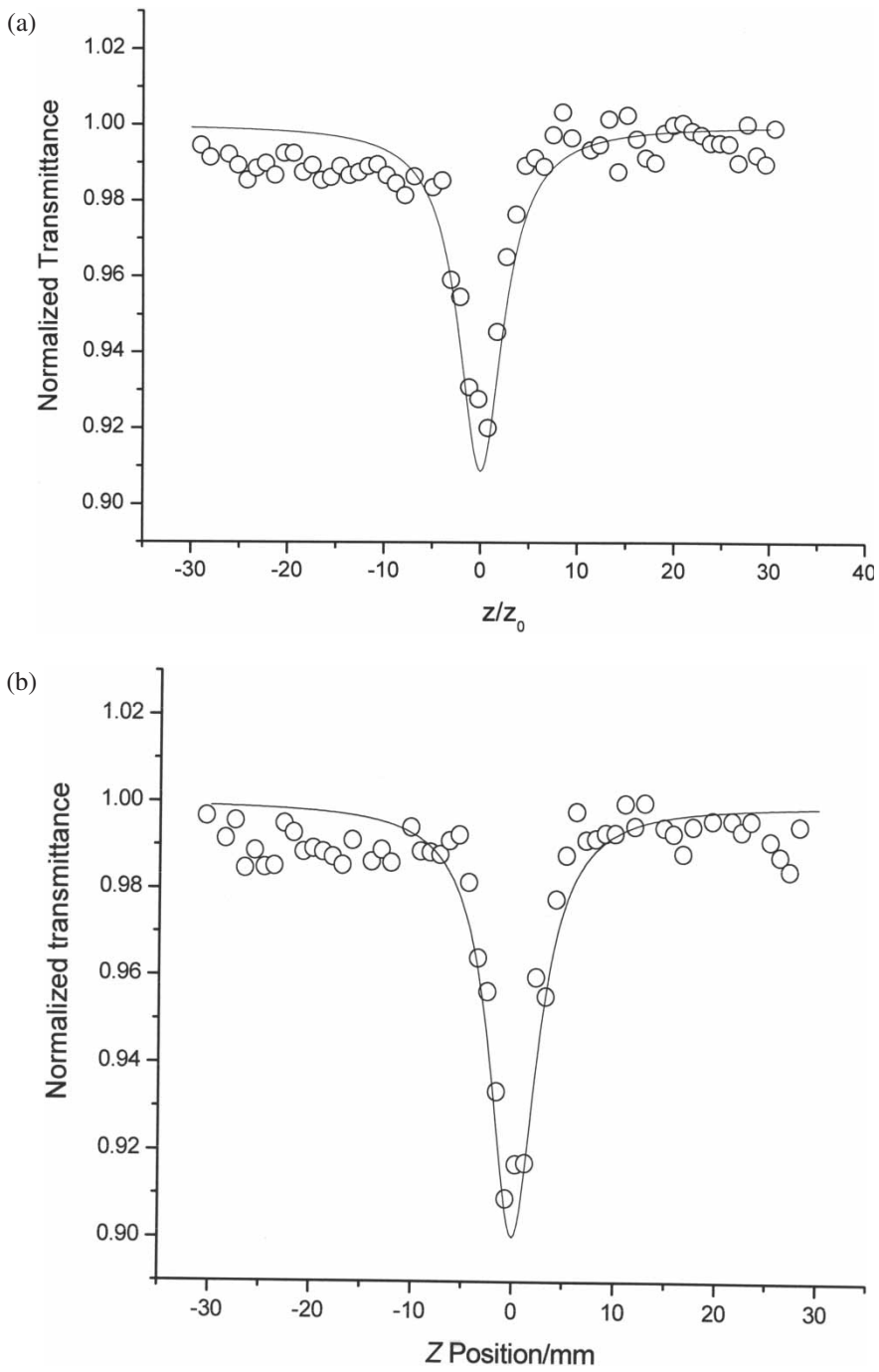


Figure 4. The third-order non-linear optical property of 1.

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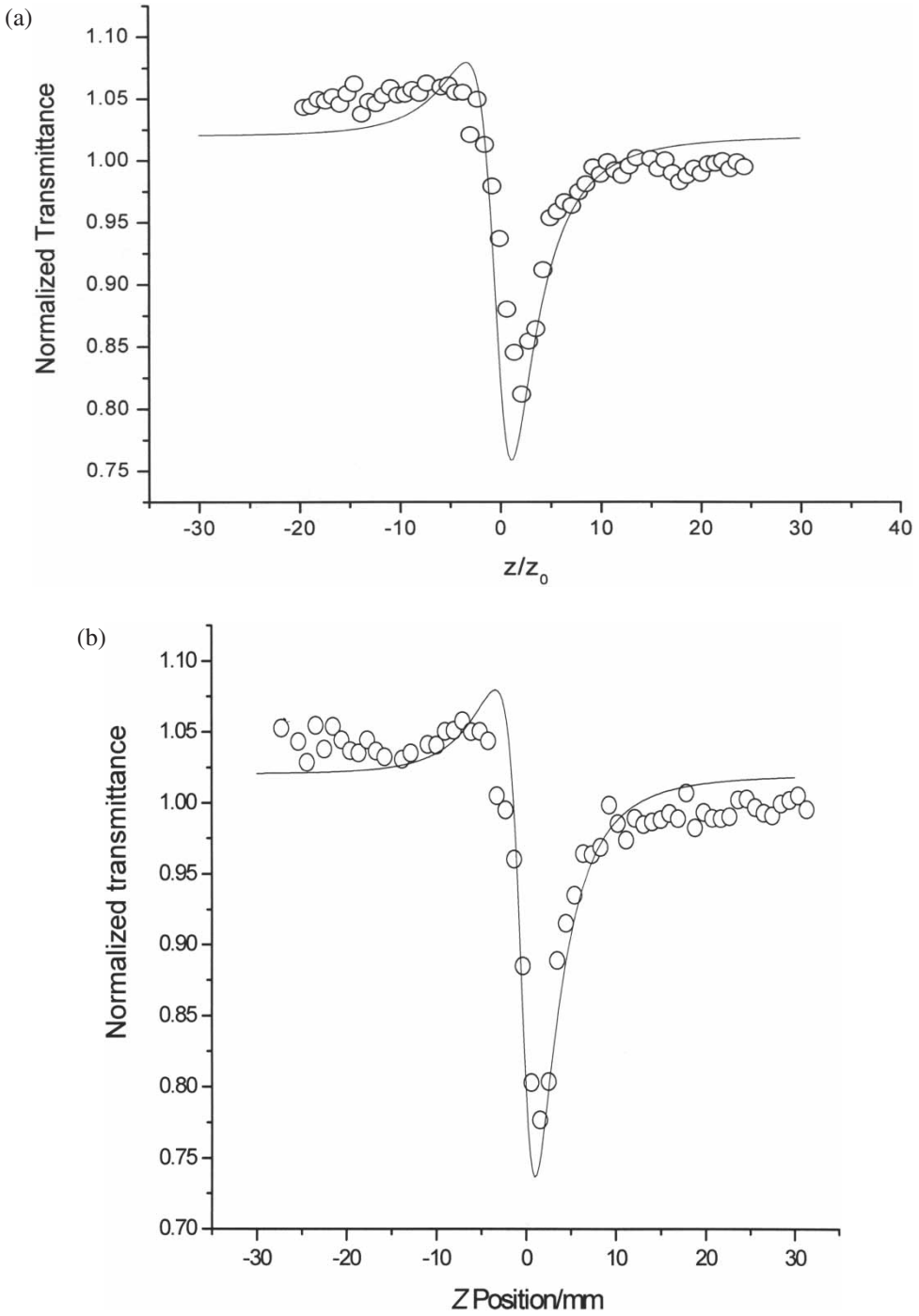


Figure 5. The third-order non-linear optical property of 2.

Table 3. Third-order non-linear optical properties of the compounds.

	α_2 (m W ⁻¹)	n_2 (m ² W ⁻¹)	χ^3 (esu)	χ^3 (esu mol ⁻¹ dm ³)	γ (esu)
1	0.09×10^{-11}	-1.76×10^{-19}	1.42×10^{-13}	1.60×10^{-10}	8.06×10^{-32}
2	0.18×10^{-11}	-3.11×10^{-19}	2.49×10^{-13}	1.96×10^{-9}	9.78×10^{-31}

attribute to C–H bending vibration. The FT-IR spectrum of complex **2** shows: 1626(w), 1608(w), 1586(w), 1515(m), 1496(w) cm⁻¹ attributed to C=C or C=N stretching vibration, 858(s), 722(s) cm⁻¹ attributed to C–H bending vibration.

3.2. The ESR spectrum

An ESR signal of **1** has been found confirming that copper atoms in **1** are Cu(II) with ESR parameter $g = 2.06$ (figure 3).

3.3. Thermogravimetric analysis

Thermogravimetric analysis proves that **1** possesses high thermal stability. In the TGA curve of **1**, there exists only one weight loss stage. From 20 to 600°C, compound **1** is stable. In the temperature range 330–640°C, the weight loss is 12.5%, corresponding to the release of *o*-phen and Cl₂. The whole weight loss (66.98%) is in good agreement with the calculated value (66.40%).

3.4. Non-linear optical (NLO) property

The third-order NLO properties of both compounds were also investigated as shown in figures 4 and 5. Both compounds exhibit the reverse saturable absorption and self-defocusing performance, but the third-order NLO property of **2** is better than **1** (table 3). Probably from π - π stacking interactions among benzene rings of **2**.

In conclusion, a new copper chloride-*o*-phen coordination complex [[CuCl] (phen)₂ [(CuCl₂)_∞] (**1**) and a three-dimensional coordination polymer [[CuCl] (phen)₂ (CuCl₂) (**2**) have been hydrothermally synthesized. Complex **1** exhibits an organic-inorganic hybrid 1D chain. The third-order NLO property of both compounds was also investigated, exhibiting reverse saturable absorption and self-defocusing performance.

Supplementary material

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters are available as supplementary crystallographic data CCDC 213831 and CCDC 213832, deposited at Cambridge Crystallographic Data Centre.

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