Formation and Nonlinear Optical Properties of a Novel Polymeric Cadmium(II) Complex Bridged by Sulfur Ions

Sheng-Li Li,[†] Jie-Ying Wu,[†] Yu-Peng Tian,*[†,††,†††] Xu-Tang Tao,[††] Min-Hua Jiang,[††] and Hoong-Kun Fun[††††]
[†]*Department of Chemistry, Anhui University, Hefei 230039, P. R. China*
[††]*State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, P. R. China*
[†††]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*
[††††]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia*

The title coordination polymer, $[Cd(NH_2NHCSNH_2)(HS)_2]_n \cdot nH_2O$, has been obtained by self-assembling from the reaction of a methanol/water (volume ratio, 1/1) solution containing cadmium chloride with equivalent amount of succinic acid and thiosemicarbazide. The X-ray crystal analysis reveals that the cadmium atoms are bridged by HS^- ligands and mutual sulfur atoms which contribute to formation of the infinite one-dimensional (1D) inorganic–organic chain in a zig-zag way. The second harmonic generation (SHG) response of the complex is much stronger than that of urea.

During recent years, there have been much attention in the design and synthesis of novel compounds with unusual and tailorable structures which are very important steps toward the discovery and fabrication of technologically useful materials.[1–3] Crystal engineering[4] based on the use of either coordinative bonds or weaker intermolecular interactions and the synthesis of low dimensional organic–inorganic hybrid materials presents an attractive new direction in solid-state chemistry.[5–7] Chemists have devoted their efforts and dreamt about the ability to assemble compounds in similar way that a bricklayer would erect a building.[8,9] It has been proven that one effective way to take advantage of the superior qualities of both inorganic and organic materials is to combine them in the same compound which is called "multifunctional hybrid materials".[10]

The discovery of the thiocyanato complexes of cadmium(II) as new NLO materials, in which the metal atoms are bridged linearly by thiocyanate ions, has already been reported.[11,12] The sulfur-bridged examples containing S^{2-}, HS^-, or S_2^{2-} ligands have also been studied,[13] but their peculiar properties have scarcely been reported. From this expectation and as our continuous work to seek novel NLO materials,[13c] we have synthesized the title complex, $[Cd(NH_2NHCSNH_2)(HS)_2]_n \cdot nH_2O$ **1**, which forms an infinite one-dimensional (1D) chained structure constructed by self-assembling and represents our first successful attempt in utilizing thiosemicarbazides and HS^- as bridging ligands to form new NLO materials. The crystal structure was determined by the single-crystal X-ray diffraction method.

Compound **1** was prepared in an methanol/water (volume ratio, 1/1) solution containing cadmium chloride with equivalent amount of succinic acid and thiosemicarbazide. The pH value must be controlled at 4.5–5.0. The mixture was stirred under reflux for 2 h and then cooled and filtered. The filtrate was left standing and evaporated slowly at room temperature. One week later, colorless single crystals suitable for X-ray structural analysis[14] were obtained (Yield: 72.5%; Anal. Calcd for **1**: C, 4.17; H, 3.13; N, 14.60%; Found: C, 4.09; H, 3.27; N, 14.78%).

In this context, we use a building-block approach of self-assembly for the synthesis of coordination polymer illustrating both
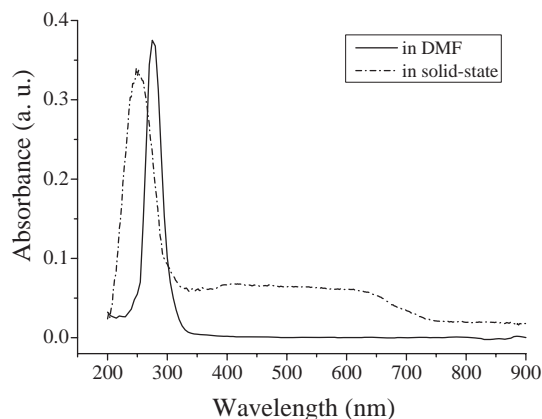

**Figure 1.** The absorption spectrum of compound **1**.

the importance of metal-ion geometry and the effect that ligand backbone can have on network construction. Such an usual synthesis method results in a novel complex with unusual structure containing bridged HS^- ions probably due to the hydrolyzation and/or decomposition of thiosemicarbazide in the hot sourish solution.[15] The crystals obtained are quite stable and show no decomposition and hygroscopic effect in air.

The electronic spectrum of compound **1** show distinctly a strong and symmetrical absorption band at ca. 275.4 nm ($\log \varepsilon = 4.67$) in DMF (dimethyl formamide) and ca. 248 nm in the solid-state (Figure 1). These bands may be attributed to the metal-mediated ligand $\pi \to \pi^*$ charge transition located on the bidentate thiosemicarbazide ligands. Such a transition is believed to be the origin of the NLO response.[12a] The compound also show a very weak absorption band in the visible region, which is only present in the solid spectra and might be assigned to the charge-transfer transition between the ligand and the cadmium, this optical absorption band is also associated with large second-order activity. On the other hand at 900 nm through 1200 nm in wavelength, the crystal had the slight additive appearance of absorption. In addition, thermogravimetric analyses (TGA) of the crystalline sample showed a total weight loss of 27.9% at 260.7 °C, indicating the formation of $CdSO_4$ (calcd 27.7%). No weight loss and melting process were recorded before this decomposition temperature, except for a slight loss of 5.9% of the sample at 163.3 °C due to the departure of the crystalline water (calcd 6.2%), suggesting the high stability of the polymeric structure.

Atom labeling and principal structural features of polymeric $[Cd(NH_2NHCSNH_2)(HS)_2]_n \cdot nH_2O$ reveal that the respective cadmium(II) atoms are 1N5S-hexacoordinated, one unidentate sulfur atom from HS^-, one nitrogen atom from a thiosemicarbazide ligand and four sulfur atoms from two bridging HS^- ions and from two adjacent thiosemicarbazide ligands, building up slightly dis-
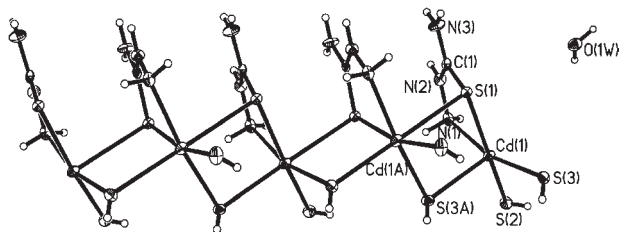
Figure 2. Structure of the one-dimensional infinite chain of **1** along the *b* axis.
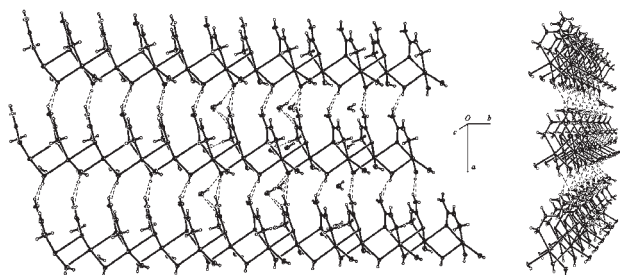
Figure 3. Projection of polymeric chains along the *b* axis (left) and *c* axis (right) of **1** crystal. Hydrogen bonds are indicated by dashed lines.

torted octahedral geometries. Neighbouring cadmium atoms are bridged by sulfur atoms from the bidentate thiosemicarbazide (N,S-chelate) and HS⁻ ligands, contributing to the formation of the one-dimensional (1D) inorganic–organic hybrid chain in a zig-zag way (Figure 2).

Coordination bond lengths of Cd(1)–N(1), Cd(1)–S(2), Cd(1)–S(1), and Cd(1)–S(3) are normal. Whereas the C–N and C–S bond distances in the thiosemicarbazide ligands are intermediate between single- and double-bond lengths, suggesting to some extent the electronic delocalization effect on the ligand upon complex formation and agreeing well with our previously synthesized compounds.[16] As illustrated in Figure 2, the thiosemicarbazide ligand in the five-membered ring of Cd(1)S(1)C(1)N(2)N(1) is almost planar [mean deviation 0.0004 Å], and such neighbouring planes are almost parallel to each other [dihedral angle between them 3.4°]. Meanwhile, the four-membered ring of Cd(1)S(1)Cd(1A)-S(3A) is also nearly planar [mean deviation 0.0027 Å] with maximum deviation of 0.0029 Å at atom Cd1, and such adjacent planes are almost vertical to each other [dihedral between them 89.2°]. Furthermore, hydrogen bonds of N–H···O(w), N–H···S, and O(w)–H(w)···S are observed which serve to link the polymeric chains and stabilize the whole supramolecular structure (Figure 3).

As a result of the unsymmetrical nature of complexes, optical activity can occur as specific physical effects.[17] Compound **1** crystallizes in space group *Cc*. Preliminary experimental results showed that the sample displayed a strong powder SHG efficiency.[18,19] The SHG efficiency of **1** crystalline powder was estimated to be ca. 20 times as large as that of urea crystalline powder by direct frequency doubling of a laser-diode at 1064 nm at room temperature. We assume that the thiosemicarbazide ligands mainly contribute to the effect, since the utilization of asymmetric ligands can introduce electronic asymmetry (push–pull effect) which is essential for a SHG response.[20]

In conclusion, the present study shows that a rational design utilizing suitable ligands and metal ions has prepared a new supramolecular polymer with nonlinear optical property. The synthetic approach is based on self-assembly of the functional components into well-defined crystalline materials, which allows important

structure–property relationships to be established.[21] X-ray diffraction analyses of **1** show that intermolecular hydrogen bonds can effectively link the 1D polymeric chains together and stabilize the molecular packings. The coordination polymer synthesized may be a promising candidate as NLO materials owing to its strong powder SHG efficiency, excellent optical transparency and considerable thermal stability. Further studies on related properties are currently under investigation.

References and Notes
1   P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, **6**, 511 (1996).
2   E. Coronado, J. R. Galanmascaros, C. Gimenezsaiz, C. J. Gomezgarcia, C. Ruizperez, and S. Triki, *Adv. Mater.*, **8**, 737 (1996).
3   D. O'Hare, *New J. Chem.*, **18**, 989 (1994).
4   A. J. Blake, N. R. Champness, P. Hubberstey, and W.-S. Li, *Coord. Chem. Rev.*, **183**, 117 (1999).
5   H. Zhang, X. Wang, H. Zhu, W. Xiao, and B. K. Teo, *J. Am. Chem. Soc.*, **119**, 5463 (1997).
6   a) S. Benard, P. Yu, J. P. Audiere, and E. Riviere, *J. Am. Chem. Soc.*, **122**, 9444 (2000). b) E. Coronado, M. Clemente-Leon, and J. R. Galan-Mascaros, *J. Chem. Soc., Dalton Trans.*, **2000**, 3955.
7   L. Martin, S. S. Turner, P. Day, and P. Guionnéau, *Inorg. Chem.*, **40**, 1363 (2001).
8   P. J. Hagrman, D. Hagrman, and J. Zubieta, *Angew. Chem., Int. Ed.*, **38**, 2638 (1999).
9   G. A. Bowmaker, B. J. Kennedy, and J. C. Reid, *Inorg. Chem.*, **37**, 3968 (1998).
10 a) D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, **35**, 1154 (1996). b) V. R. Thalladi, S. Brasselet, H. Weiss, D. Blaser, and A. K. Katz, *J. Am. Chem. Soc.*, **120**, 2563 (1998).
11 a) D. R. Yuan, D. Xu, M. G. Liu, Q. Fang, and W. T. Yu, *Appl. Phys. Lett.*, **70**, 1 (1997). b) X. Q. Wang, D. Xu, M. K. Lu, D. R. Yuan, G. H. Zhang, and Y. P. Tian, *Mater. Res. Bull.*, **36**, 1287 (2001).
12 a) H. Zhang, X. Wang, K. Zhang, and B. K. Teo, *Coord. Chem. Rev.*, **183**, 157 (1999). b) M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **62**, 424 (1989).
13 a) R. J. Pleus, H. Waden, W. Saak, D. Haase, and S. Pohl, *J. Chem. Soc., Dalton Trans.*, **1999**, 2601. b) J. R. Anacona, M. Azocar, O. Nusetti, and C. R. Barbarin, *Transition Met. Chem.*, **28**, 24 (2003). c) S. L. Li, J. Y. Wu, X. J. Zhang, Y. P. Tian, M. H. Jiang, Z. Y. Chen, A. Usman, and H. K. Fun, *Chem. Lett.*, **32**, 748 (2003).
14 Crystal data for **1**: CH₉CdN₃OS₃ $M_r = 287.73$, monoclinic, *Cc*, $a = 10.1257(7)$ Å, $b = 13.9350(10)$ Å, $c = 6.8968(5)$ Å, $\beta = 124.0950(10)°$, $V = 805.87(10)$ Å³, $Z = 4$, $D_{calcd} = 2.371$ g cm⁻³, Mo Kα, $T = 293(2)$ K, A total of 2428 reflections were measured. $R_1 = 0.0563$, and $wR_2 = 0.1416$ for 1432 observed reflections with $I > 2\sigma(I)$. Min. and Max. resd. dens. are $-2.41(4)$ and $1.92(9)$ e·A⁻³, respectively.
15 a) Q. Y. Lu, F. Gao, and D. Y. Zhao, *Nano Lett.*, **2**, 725 (2002). b) J. Wu, Y. Jiang, Q. Li, X. M. Liu, and Y. T. Qian, *J. Cryst. Growth*, **235**, 421 (2002).
16 a) S. L. Li, A. Usman, I. A. Razak, H. K. Fun, J. Y. Wu, Y. P. Tian, M. H. Jiang, and Z. Y. Chen, *Acta Crystallogr.*, **C59**, m181 (2003). b) S. L. Li, A. Usman, I. A. Razak, A. A. Rahman, H. K. Fun, J. Y. Wu, Y. P. Tian, M. H. Jiang, and Z. Y. Chen, *Acta Crystallogr.*, **E59**, m199 (2003).
17 T. Hahn and H. Klapper, "International Tables for Crystallography," Reidel, Dordrecht, The Netherlands (1993), Vol. A, Chap. 10.5, p 780.
18 The SHG intensity was determined by the powder technique of Kurtz and Perry, in which the second harmonic output was generated by irradiating powder samples of randomly oriented crystallites. The incident radiation came from a Q-switched and mode-locked Nd:YAG laser. The 532 nm second harmonic intensity of **1** crystalline powder was estimated to be ca. 20 times as large as that of urea crystalline powder by direct frequency doubling of a laser-diode at 1064 nm at room temperature. The fact should be emphasized that the present result is very preliminary and the value evaluated by the powder measurement is rough and not reliable. Further measurements to obtain accurate values of the macroscopic second-order susceptibility (χ) are considerable.
19 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, **39**, 3798 (1968).
20 a) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, **37**, 1461 (1998). b) O. R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong, and W. Lin, *Angew. Chem., Int. Ed.*, **38**, 536 (1999).
21 a) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **29**, 1304 (1990). b) J.-M. Lehn, "Supramolecular Chemistry," VCH, Weinheim (1995).