研究简报

具有平面结构的四齿肼基硫代甲酸苄酯席夫碱镍配合物的合成，晶体结构和三阶非线性光学性质研究

周建豪[1] 王玉晓[2] 陈学太*,[1] 宋瑛林[2] 翁林红[3] 游效曾[1]

([1]南京大学配位化学国家重点实验室，配位化学研究所，南京 210093)

([2]哈尔滨工业大学应用物理系，哈尔滨 150001)

([3]复旦大学化学系，上海 200433)

关键词: 镍 平面结构 晶体结构 三阶非线性光学

分类号: O611.6 O614.81+3

Synthesis, Structure and Third-Order Nonlinear Optical Properties of a Planar Nickel Complex with Rigid Quadridentate Schiff Base Derived from S-benzyl Dithiocarbazate

ZHOU Jian-Hao[1] WANG Yu-Xiao[2] CHEN Xue-Tai*,[1]

SONG Ying-Lin[2] WENG Lin-Hong[3] YOU Xiao-Zeng[1]

([1] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing* 210093)

([2] *Department of Applied Physics, Harbin Institute of Technology, Harbin* 150001)

([3] *Department of Chemistry, Fudan University, Shanghai* 200433)

A planar metal complex NiL, H_2L = acenaphthenequinone bis(S-benzyldithiocarbazate), **1**, has been prepared via the template effect of nickel ion. Crystal structure of **1** was determined by X-ray diffraction analysis and shows the planar coordination configuration around the central nickel atom. *Z*-scan measurements show that **1** is a transition metal complex exhibiting high third-order nonlinear optical effect.

Keywords: nickel planar structure crystal structure third-order nonlinear optics

0 Introduction

There is currently intense research interest in developing new nonlinear materials with high third-order nonlinear optical effects due to their potential applications in a number of important technologies including optical power limiting for sensor protection, optical switches, all optical signal processing and optical computing[1-3]. Metal complexes with planar, π-conjugated tetradentate or bidentate ligand are of particular interest because they contain both electrons that are free to move within the π extended system of the ligands and the additional energy levels introduced by the presence of metal ions, among which the most extensively studied are phthalocyanine derivatives[4,5] and metal dithiolenes et al[6,7]. Recently research has been focused on

收稿日期：2001-11-09。收修改稿日期：2002-03-05。

国家自然科学基金资助项目(No. 20028101)和江苏省自然科学基金资助项目(No. BK99032)。

*通讯联系人。E-mail: xuetai@jlonline.com

第一作者：周建豪，男，26岁，硕士研究生；研究方向：功能配合物。

search for new types of molecular materials with high third-order nonlinear properties and to develop the structure-property relationship. Some planar metal complexes with N_2S_2 coordination environment have been shown to exhibit large third-order nonlinear optical properties[8-10]. Here we report synthesis, structure and third-order nonlinear optical properties of planar transition metal complex NiL, H_2L = acenaphthenequinone bis(S-benzyldithiocarbazate), **1**. It is expected that the introduction of a rigid naphthalene backbone into quadridentate Schiff base derived from S-benzyl dithiocarbazate would lead to the exact planar structure and it is of interest to investigate their third-order nonlinear optical properties.

1 Experimental

1.1 Synthesis

All chemicals are commercially available and used without further purification.

Acenaphthenequinone (0.048g, 0.25mmol) was dissolved in absolute EtOH (30mL) under stirring and heated to reflux. S-benzyldithiocarbazate (0.099g, 0.50mmol) and $NiCl_2 \cdot 6H_2O$(0.0593g, 0.25mmol) were added to the solution and then refluxed for 5 hs. The resulting precipitates were collected and recrystallized from DMF to give a pure crystalline sample of **1**. Yield: 85%. ^1H NMR(d_7-DMF): 8.30 ~ 7.86, m (6H, $C_{10}H_6$), 7.55 ~ 7.33, m (5H, C_6H_5), 4.66, s (2H, CH_2). IR (KBr cm^{-1}): 1605 (m, C = C), 1566 (m, CN), 1069 (s, CS). Calcd. for $C_{28}H_{20}N_4NiS_4$: C, 56.11; H, 3.36; N, 9.35. Found: C, 56.22; H, 3.54; N, 9.46.

1.2 Crystal Data for 1

A needle-like deep-brown crystal of **1** with dimensions 0.35 × 0.02 × 0.02mm^3 was used for structural analysis at 293K on Siemens CCD SMART system using Mo$K\alpha$ radiation (λ = 0.71073Å). Crystal data: $C_{28}H_{20}N_4NiS_4$, F_w = 599.43, Monoclinic, space group $P2_1/c$, a = 24.600(17), b = 11.782(8), c = 9.115(6) Å, β = 95.776(10)°, V = 2628(3) Å^3, D_{cal} = 1.515g · cm^{-3}, Z = 4. A total of 10465 reflections are collected, of which 4622 reflections are unique. The structure was solved by direct methods and refined by full-least-squares method using SHELX-97 program set[11], converging to R_1 = 0.0672 and wR_2 = 0.1134 ($I > 2\sigma(I)$).

CCDC: 180869.

1.3 Nonlinear Optical Properties

UV-Vis spectra were recorded on a UV-3100 spectrometer.

The nonlinear optical properties of the DMF solution with concentration of 3.3 × 10^{-4}mol · L^{-1} were measured by the Z-scan technique at 532 nm using a Continuum ns/ps Nd: YAG laser system with pulse width of 10 ns. The spot radius of the laser beam was measured to be 45μm. The input and the output energies of beams were measured with an energy meter (Laser Precision Corporation Rjp-735). The focal length of lens was 300mm. The experimental data were collected by utilizing a single shot at a rate of 1 pulse per minute to avoid the influence of thermal effect. The input pulse energies are 180μJ. It was filled into a 2 mm-thick cuvette with a linear transmittance of 95%.

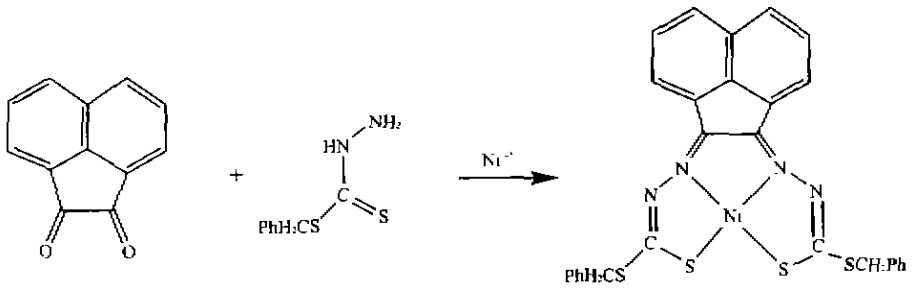
2 Results and Discussions

1 was prepared by metal-ion template effect, i.e., the treatment of acenaphthenequinone and S-benzyl dithiocarbazate in the presence of nickel ion, see Scheme 1. The free ligand could not be obtained by the condensation reaction between acenaphthenequinone and S-benzyl dithiocarbazate. In our hands, only mono-condensation product was obtained in the presence of catalytic amount of acid in the absence of metal ion.

2.1 Crystal Structure

The molecular structure of **1** is shown in Fig. 1 and the selected bond lengths and bond angles are listed in Table 1. The coordination geometry around Ni (Ⅱ) is nearly planar with normal Ni-S distances (av. 1.884Å) and Ni-N distances (av. 2.171Å). The three five-membered chelate angles N(1)-Ni(1)-S(1), N(3)-Ni(1)-N(1), N(3)-Ni(1)-S(3), are 86.27°, 85.11°, 85.53°, respectively while angle S(1)-Ni-S(3) is 103.13°. The molecule has C_2 symmetry with a C_2 axis passing through the nickel atom and the middle point of C(1)-C(11). The two outer benzyl groups are situated up and down with respect to the central coordination plane.

The full molecule except the outer two benzyl



Scheme 1

Table 1　Selected Bond Lengths (Å) and Angles (°) for 1

Ni(1)-N(3)	1.880(4)	Ni(1)-N(1)	1.887(4)	Ni(1)-S(3)	2.1690(18)
Ni(1)-S(1)	2.1730(18)	S(1)-C(13)	1.767(5)	S(2)-C(13)	1.736(5)
S(3)-C(21)	1.761(6)	S(4)-C(21)	1.740(5)	N(1)-C(1)	1.302(6)
N(1)-N(2)	1.382(5)	N(2)-C(13)	1.304(6)	N(3)-C(11)	1.304(6)
N(3)-N(4)	1.374(5)	N(4)-C(21)	1.307(6)	C(1)-C(11)	1.466(7)
C(1)-C(2)	1.473(7)	C(10)-C(11)	1.470(7)		
N(3)-Ni(1)-N(1)	85.11(19)	N(3)-Ni(1)-S(3)	85.53(14)	N(1)-Ni(1)-S(3)	170.57(14)
N(3)-Ni(1)-S(1)	171.02(13)	N(1)-Ni(1)-S(1)	86.27(14)	S(3)-Ni(1)-S(1)	103.13(8)
C(13)-S(1)-Ni(1)	94.65(19)	C(21)-S(3)-Ni(1)	95.02(19)	C(1)-N(1)-N(2)	122.4(4)
C(1)-N(1)-Ni(1)	133.0(4)	N(2)-N(1)-Ni(1)	124.5(3)	C(13)-N(2)-N(1)	109.7(4)
C(11)-N(3)-N(4)	121.3(4)	C(11)-N(3)-Ni(1)	132.8(4)	N(4)-N(3)-Ni(1)	125.8(3)
C(21)-N(4)-N(3)	108.8(4)	N(1)-C(1)-C(11)	114.2(5)	N(1)-C(1)-C(2)	137.3(5)
C(11)-C(1)-C(2)	108.4(4)	N(3)-C(11)-C(1)	114.9(5)	N(3)-C(11)-C(10)	136.7(5)
C(1)-C(11)-C(10)	108.4(4)	N(2)-C(13)-S(2)	121.9(4)	N(2)-C(13)-S(1)	124.8(4)
S(2)-C(13)-S(1)	113.3(3)	N(4)-C(21)-S(4)	121.1(4)	N(4)-C(21)-S(3)	124.7(4)
S(4)-C(21)-S(3)	114.2(3)				

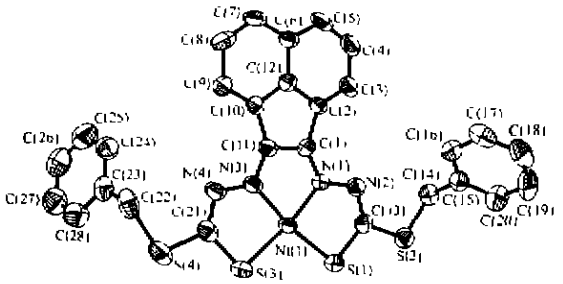


Fig. 1　Molecular structure of **1**

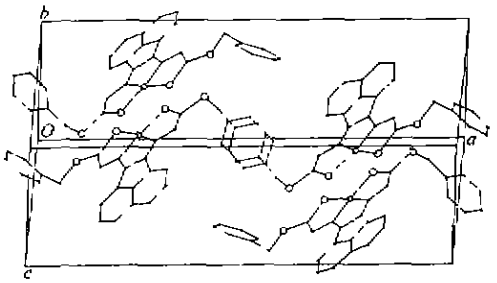


Fig. 2　Crystal packing of **1**

groups is nearly planar. The crystal packing in the unit cell is shown in Fig. 2. The molecules pack together through aromatic interactions via phenyl-phenyl stacking and face-face interaction between the central molecular planes with a distance of 3.5Å.

2.2　Nonlinear Optical Properties

The electronic spectrum of **1** in DMF solution shows there is low absorption in the visible and near-infrared regions, see Fig. 3. Z-scan measurements were carried out to investigate the third-order nonlinear optical properties of **1**. The Z-scan results shown in Fig. 4(a) are the Z-scan data measured without the aperture while those in Fig. 4(b) were the results under the close aperture($S=0.15$). To obtain the NLO parameters we employed a *Z*-scan theory[12], which considers nonlinearities of third-order nature. The theoretical simulation leads to the estimation of nonlinear absorption coefficient $\alpha_2 = 5.6 \times 10^{-12}\text{m} \cdot \text{W}^{-1}$. The peak-valley pattern of the normalized transmittance curve obtained under the close aperture configuration shows that **1** has a negative sign for refractive nonlinearity and exhibits a self-focusing effect. A calculated

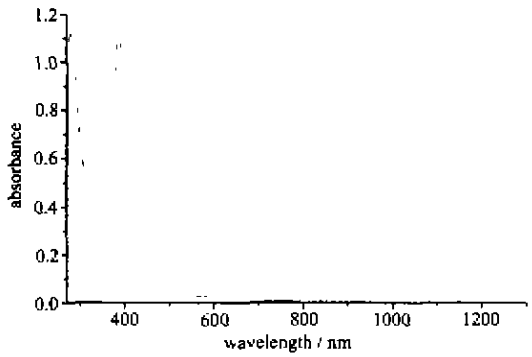


Fig. 3 UV-VIS-NIR spectra of complexes NiL (2.7×10^{-5} mol · L^{-1}) in DMF solution
The optical path length is 1cm.

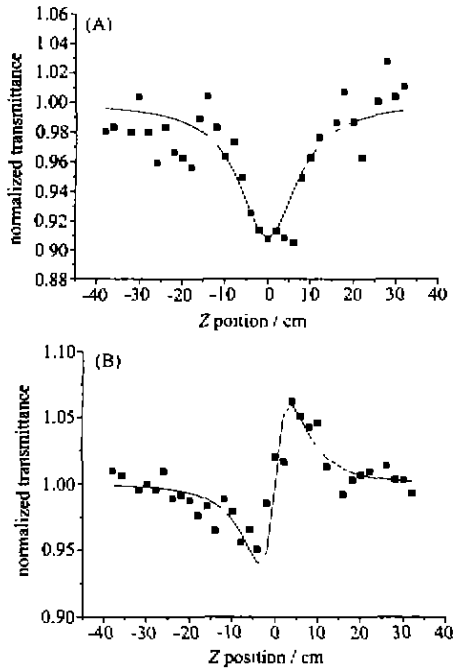


Fig. 4 *Z*-scan data of 1 (a) Data collected under the open aperture configuration showing small NLO absorption, (b) Data collected under the closed aperture configuration showing self-focusing effect
The sold lines are the simulated curves

curve is obtained according to the theory of *Z*-scan, leading to nonlinear refractive index $n_2 = 6.34 \times 10^{-12}$ esu. The good agreement between the experimental data and theoretical curve indicates that the nonlinearity is mainly of third-order in nature, shown in Fig. 4. Since the contribution of the nonlinear absorption is much smaller than that of nonlinear refraction, nonlinear properties of 1 is dominated by nonlinear refraction. The third-order NLO susceptibility of **1**, $\chi^{(3)} = n_2 = 6.34 \times 10^{-12}$esu, which indicates that 1 is very promising nonlinear refraction material. The measured susceptibilty of **1** can be comparable to those of metal dithiolenes[6, 7] and other metal complexes with N_2S_2 coordination enviroments[8 ~ 10].

To conclude, the metal complex with rigid quadridentate Schiff base derived from S-benzyl dithiocarbazate exhibits high third-order nonlinear optical effect. It is expected that the variation of metal ions and rigid backbone will lead to more transition metal complexes exhibiting nonlinear optical effect and provide more data to reveal the structure-property relationship.

Acknowledgements: This work is financially supported by the research grants from National Natural Science Foundation of China (20028101), Natural Science Foundation of Jiangsu Province (BK99032).

References

[1] Nalwa H. S., Miyata S. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press: Orlando, **1997**.

[2] Marder S. R., Sohn J. E., Stucky G. S. *Materials for Nonlinear Optics, Chemical Perspectives, ACS Symposium Series*, *Vol.* 455, American Chemical Society: Washington, **1991**.

[3] Long N. J. *Angew. Chem. Int. Ed. Engl.*, **1995, 34**, 21.

[4] Perry J. M., Mansour K., Lee I. Y. S., Wu X. L., Bedworth P. V., Chen C. T., Ng D., Marder S. R., Miles P., Wada T., Tian M., Sasabe H. *Science*, **1996, 273**, 1533.

[5] De La Torre G., Vázquez P., Agulló-López F., Torres T. *J. Mater. Chem.*, **1997, 8**, 1671.

[6] Oliver S., Winter C. *Adv. Mater.*, **1992, 4**, 119.

[7] Zuo J. L., Yao T. M., You F., You X. Z., Fun H. K., Yip B. C. *J. Mater. Chem.*, **1996, 6**, 1633.

[8] Zhu X. H., Chen X. F., Zhang Y., You X. Z., Tan W. L., Ji W., Vittal J. J., Tan G. K., Kennard C. H. L. *New J. Chem.*, **2000, 24**, 419.

[9] WU Jie-Ying(吴杰颖), TIAN Yu-Peng(田玉鹏), ZHANG Yin-Han(张银汉), DUAN Chun-Ying(段春迎), XIE Fu-Xin(谢复新), NI Shi-Sheng(倪诗圣) *Huaxue Xuebao* (*Acta Chimica Sinica*), **1999, 57**, 202.

[10] Duan C. Y., Tian Y. P., Lu Z. L., You X. Z., Mak T. C. W. *J. Coord. Chem.*, **1998, 46**, 59.

[11] Sheldrick G. M. *SHELX-97*, *Release* 97-2, *University of Göttingen*, Germany, **1998**.

[12] Sheik-Bathae M., Said A. A., Wei T. H., Hagan D. J., Van Stryland E. W. *IEEE J. Quant. Electron*, **1990, 26**, 760.