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Synthesis, characterization and optical limiting effect of nickel complexes of multi-sulfur 1,2-dithiolene

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Abstract

Three nickel complexes with a new multi-sulfur 1,2-dithiolene ligand, $(n-Bu_4N)[Ni(cddt)_2]$ **1**, $(Ph_4P)[Ni(cddt)_2]$ **2** and $[Ni(cddt)_2]$ **3** (cddt=4a, 6, 7, 7a-5H-cyclopenta[b]-1,4-dithiin-2,3-dithiolate), have been synthesized and characterized by electrochemical measurements, IR, EPR and UV–Vis-NIR spectroscopies. The crystal structure of complex **2** is determined. Their optical nonlinearities are measured by the Z-scan technique with an 8 ns pulsed laser at 532 nm and all exhibit NLO absorptive abilities. Complexes **1** and **2** both exhibit effective self-defocusing performance ($n_2 = -5.81 \times 10^{-10}$ esu for **1** and -4.51×10^{-10} esu for **2**). The optical limiting (OL) effects were observed with nanosecond and picosecond laser pulses. The OL capability of complex **3** is superior to C₆₀ at the same experimental condition in ns measurements.

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1. Introduction

In recent years, bis-1,2-dithiolene complexes of transition metals have been widely studied due to their interesting properties and applications in areas such as conductivity, magnetism, non-linear materials and catalysis [1-15]. They have larger delocalized systems and can exist in several clearly defined oxidation states. Also they exhibit high thermal and photochemical stabilities. The third-order optical nonlinearity and the optical limiting (OL) ability of nickel complexes with multi-sulfur 1,2-dithiolene ligands have been investigated by our group previously [9,10]. An ideal optical limiter should have the capability of being transparent under laser radiation of low energies and opaque at high energies. The most frequently reported materials are fullerenes (C₆₀) [16–22], and phthalocyanine complexes

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[23–32], which are generally regarded as the best candidates for optical limiting application. As part of our continued work on exploring better OL materials, we report here the synthesis and properties of three new nickel complexes based on a new multi-sulfur dithiolene ligand, 4a, 6, 7, 7a-5H-cyclopenta[b]-1, 4-dithiin-2, 3-dithiolate (cddt). The nickel complexes exhibit excellent optical limiting effects towards nanosecond and picosecond laser pulses. In this paper, the crystal structure of $Ph_4P[Ni(cddt)_2]$ **2** is also presented.

2. Experimental

2.1. Synthesis

All solvents were of analytical grade and used without further purification. All reactions were carried out under N₂. The ligand precursor, cis-4a, 6, 7, 7a-tetrahydro-5H-cyclopenta[b]-1, 3-dithiolo[4, 5-e][1,4]dithiin-2-thione was

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prepared by the (2+4) cycloaddition reaction as described in the literature [33].

2.1.1. Preparation of $(n-Bu_4N)[Ni(cddt)_2]$ (1)

Potassium hydroxide (2.0 g, 35.7 mmol) and cis-4a, 6, 7, 7a-tetrahydro-5H-cyclopenta[b]-1,3-dithiolo[4,5-e][1,4] dithiin-2-thione (1.0 g, 3.8 mmol) were added to 20 mL of ethanol. The reaction mixture was stirred for 1 h at 40 °C. The resulting pale yellow microcrystals of K₂cddt were isolated by centrifugation. Then it was dissolved instantly in methanol (20 mL). A solution of NiCl₂·2H₂O (0.45 g, 1.9 mmol) in 20 mL of methanol was added dropwise to this solution. After stirring at room temperature for 30 min, the solution was then exposed to air for 15 min. After filtration, 1 equiv. of tetrabutylammonium bromide was added to the filtrate, and dark green solids were precipitated immediately. The solids were collected by filtration and then recrystallized from acetone. The yield was 0.99g (70%). Anal. Calc. for C₃₀H₅₂NNiS₈ (%): C, 48.58; H, 7.01; N, 1.88; Ni, 7.91. Found: C, 47.92; H, 6.85; N, 1.82; Ni, 8.27. FT-IR (KBr, cm⁻¹): 2953(m), 1459(m), 1438(m), 1373(s), 881(m).

2.1.2. Preparation of (Ph_4P) [Ni(cddt)₂] (2)

This complex was synthesized by mixing **1** with excess Ph_4PBr in CH_3CN . The green precipitate was collected by filtration and washed with methanol and ether, and then dried in vacuo. The yield was 0.42 g (75%). Anal. Calc. for $C_{38}H_{36}NiPS_8$ (%): C, 54.44; H, 4.32; Ni, 7.00. Found: C, 53.75; H, 4.25; Ni, 7.26. FT-IR (KBr, cm⁻¹): 3050(w), 2926(m), 1624(m), 1437(m), 1374(s), 1108(s), 723(s), 688(s).

2.1.3. Preparation of $[Ni(cddt)_2]$ (3)

This complex was prepared by the reaction of **1** and excess iodine in acetone. The black precipitate was collected by filtration and washed with methanol and ether, and then dried in vacuo. The yield was 0.28 g (80%). Anal. Calc. for $C_{14}H_{16}NiS_8$ (%): C, 33.67; H, 3.23; Ni, 11.75. Found: C, 32.89; H, 3.45; Ni, 11.66. FT-IR (KBr, cm⁻¹): 2953(m), 1624(m), 1443(m), 1263(s), 1231(s), 1186(s), 824(m).

2.2. Physical measurements

CHN analyses were performed using a Perkin-Elmer 240C analytical instrument. Ni element analysis was measured on a Jarrell-ash ICP quantimeter. IR spectra were collected on a Shimadzu 440 spectrometer with KBr pellets. The cyclic voltammetry was performed by a model 79-1V-Analyser with a electrochemical cell using a platinum wire as the working electrode, a platinum plate as auxiliary electrode and Ag/AgCl as reference electrode. Measurements were made in CH_2Cl_2 using 0.4 M tetrabutylammonium perchlorate as the supporting electrolyte, and nitrogen was passed for 15 min prior to each

measurement. UV–VIS spectra were recorded on a UV-3100 spectrophotometer. The ESR spectrum was recorded on a Bruker ER 200-D-SRC spectrometer.

2.3. Structure determination

Green crystals of 2 were obtained upon recrystallization from CH₂Cl₂ and CH₃OH. Intensities data were measured on a Bruker Appex CCD diffractometer with monochromated Mo-K_{α} (λ =0.71073 Å) and processed using Smart [34]. The structure was solved by direct methods. It belongs to the triclinic system, P-1 space group. The cell constants are a = 10.474(2), b = 12.975(2), c = 16.237(2) $\alpha = 86.60(1), \quad \beta = 71.25(1), \quad \gamma = 66.52(1)^{\circ}, \quad V =$ Á, 1910.5(6) $Å^3$, which were confirmed in the subsequent refinement. The structure was refined using the SHELXTL [34] program package. All non-hydrogen atoms were refined anistropically by full-matrix least squares. The hydrogen atoms were placed in their calculated positions with C-H=0.93–0.96 Å. All the hydrogen atoms were assigned fixed isotropic thermal parameters (1.2-1.5 times of the atom they attached), and allowed to ride on their respective parent atoms. A full-matrix least squares calculation using 4437 unique reflections $(I > 2.0\sigma (I))$ gave a final refinement with *R* factors of R = 0.0533 and $R_w = 0.1386$.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 185926. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336033; e-mail to: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

2.4. Optical measurements

Complexes 1 and 2 were dissolved in DMF (the neutral complex 3 in toluene) and contained in 5-mm-thick quartz cells for the measurements of third-order nonlinear optical properties and optical limiting effects, which were performed with linearly polarized 8 ns pulsed at 532 nm generated from a Q-switched frequency-doubled Nd:YAG laser. Three complexes are all stable toward air and laser light under experimental conditions. The spatial profiles of the optical pulses were of nearly Gaussian transverse mode. The pulsed laser was focused onto the sample cell with a 30 cm focal length mirror. The energy of input and output pulses was measured simultaneously by precision laser detectors (818J-09B, Newport Corp.), which were linked to a computer by a New-port Com. Attenuator. The experimental data were collected utilizing a single shot at a rate of 1 pulse per second to avoid the influence of thermal and long-term effects.

The third-order NLO absorptive and refractive properties of these complexes were determined by performing Z-scan measurements [35]. The samples were mounted on a computer-controlled translation stage moving along





the Z-direction with respect to the focal point instead of being positioned at its focal point. To determine both the sign and magnitude of the nonlinear refraction, a 2 mm diameter aperture was placed in front of the transmission detector and the transmittance recorded as a function of the sample position on the Z-axis (closed-aperture Z-scan). To measure the nonlinear absorption, the Z-dependent sample transmittance was recorded without the aperture (open aperture Z-scan).

3. Results and discussion

3.1. Synthesis

The synthesis of complex 1 and 3 is outlined in Scheme 1. The electrochemistry of the complex anion $[Ni(cddt)_2]^$ in 1 is investigated by cyclic voltammetry in CH₂Cl₂.



Fig. 1. UV–VIS-NIR spectra of complex 2 (1.08×10^{-4} M) in CH₃CN (–) and complex 3 (4×10^{-5} M) in C₆H₆ (–) at 25 °C.



Fig. 2. Perspective view of $[Ni(cddt)_2]^-$ with atom numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

It shows three redox couples in the recorded region: the first one-electron reduction assigned to $[\text{Ni}(\text{cddt})_2]^2$ / $[\text{Ni}(\text{cddt})_2]^-$ is quasi-reversible $(E_{1/2} = -0.69 \text{ V})$; the second reversible peak $(E_{1/2} = 0.08 \text{ V})$ is assigned to $[\text{Ni}(\text{cddt})_2]^-/[\text{Ni}(\text{cddt})_2]$; the third quasi-reversible peak is also observed at a more positive potential $(E_{1/2} = 0.92 \text{ V})$, which can be reasonably assigned to oxidation of the ligand.

The frozen-glass ESR spectrum of complex **2** in DMF at 128 K shows three peaks with $g_1=2.114$, $g_2=2.050$, $g_3=1.998$, which are closer to the values of similar nicklel-dithiolene complexes [10].

The UV–Vis-NIR spectra of $(Ph_4P)[Ni(cddt)_2]$ **2** and $[Ni(cddt)_2]$ **3** are shown in Fig. 1. Complex **2** in acetonitrile solution shows a strong broad absorption at 1034 nm (ε =11500), which is assigned to a $\pi \rightarrow \pi^*$ transition $(2b_{1u} \rightarrow 3b_{2g})$ [5]. Complex **3** in benzene solution exhibits this absorption at 982 nm (ε =46000). Such a strong intensity is perhaps due to the strongly coordinated donors in the ligands.

3.2. Crystal structure of complex 2

The molecular structure of $(Ph_4P)[Ni(cddt)_2]$ **2** with atom numbering scheme is shown in Fig. 2, and selected bond distances and angles are listed in Table 1.

The four S atoms surround the Ni atom to give a squareplanar geometry with nearly equal Ni–S bond lengths

Table 1 Selected bond distances (Å) and angles (°) in $(Ph_4P)[Ni(cddt)_2]$ 2						
Ni1-S2	2.150(1)	Ni1-S1	2.156(1)			
S1-C1	1.739(5)	S2-C2	1.731(5)			
S3-C1	1.750(5)	S3-C3	1.803(5)			
S4-C2	1.744(5)	S4-C7	1.824(5)			
C1-C2	1.352(7)	C3-C4	1.51(1)			
C3–C7	1.512(7)	C4–C5	1.49(1)			
C5-C6	1.45(1)	C6–C7	1.525(7)			
S1-Ni1-S2	91.91(4)	Ni1-S1-C1	103.6(2)			
Ni1-S2-C2	103.8(2)	C1-S3-C3	104.4(2)			
C2-S4-C7	99.5(2)	S1-C1-C2	119.9(4)			
S1-C1-S3	116.9(3)	S3-C1-C2	122.9(4)			
S4-C7-C3	115.0(4)	S2-C2-S4	118.8(3)			
S2-C2-C1	120.3(4)	S4-C2-C1	120.9(4)			
S3-C3-C7	117.6(3)	C4-C3-C7	107.1(5)			
S3-C3-C4	109.3(5)	C3-C4-C5	105.6(6)			
C4-C5-C6	110.7(6)	C5-C6-C7	107.0(5)			
C3–C7–C6	105.3(4)	S4-C7-C6	108.0(4)			



Fig. 3. Packing diagram of 2 looking down the a axis.

and S–Ni–S angles. The Ni atom lies at the origin, and the $S_2C=CS_2$ unit in the cddt ligand is planar. The gross geometry of $[Ni(cddt)_2]^-$ is very similar to that of $[Ni(ddt_2)]^-$ [15]. The average C–S, Ni–S and C=C bond lengths are 1.735(5), 2.153(1) and 1.352(7) Å, respectively. The corresponding values in the (Bu₄N) [Ni(dddt)₂] are 1.75, 2.137 and 1.37 Å [15]. The difference in bond lengths can be explained as the result of steric and electronic effects of the external units of the ligand. The cyclopentene ring adopts an envelope conformation with the *trans* orientation.

Owning to the planar geometry, the $[Ni(cddt)_2]^-$ units can be stacked along the *a*-axis to generate columns which are separated from one another by Ph₄P⁺ ions, as shown in Fig. 3. The closest Ni…Ni distance is 10.474(2) Å, which is the length of the *a* axis. The shortest intermolecular S…S contact of 5.019(3) Å occurs between S3 and S5, which is larger than the sum of the van der Waals radii (3.70 Å) [36].

3.3. Nonlinear optical absorption and refraction

The third-order nonlinear optical properties of the three complexes were investigated with 532 nm laser pulses of 8 ns duration ($I_0 = 4.48 \times 10^{12}$ W m⁻²) in each solution, respectively. The results from the Z-scan experiments [34] for these three complexes are summarized in Table 2. Typical results from the Z-scan experiments for complexes **3** are displayed in Fig. 4. The nonlinear absorption components were evaluated by the Z-scan method under an aperture configuration and the NLO absorptive experimental data for complexes **1–3** obtained under

the conditions used in this work, can be represented by equations (1) and (2) [35,37]:

$$T(z) = \frac{1}{\sqrt{\pi}q(z)} \int_{-\infty}^{+\infty} \ln[1 + q(z)e^{-\tau^2}] d\tau$$
(1)

$$q(z) = \int_{-\infty}^{+\infty} \int_{0}^{+\infty} \alpha_2 \left(\frac{I_0}{1 + (z/z_0)^2} \right) e^{[-2(r/\omega_0)^2 - (t/t_0)^2]} \\ \times \left(\frac{1 - e^{-\alpha_0 L}}{\alpha_0} \right) r \, \mathrm{d}r \, \mathrm{d}t$$
(2)

where light transmittance, *T*, is a function of the sample's *Z*-position (against focal point z=0), *z* is the distance of the sample from the focal point, *L* is the sample thickness, I_0 is the peak irradiation intensity at focus, $z_0 = \pi \omega_0^2 / \lambda$ (where ω_0 is the spot radius of the laser pulse at focus and λ is the laser wave length), *r* is the radial coordinate, *t* is the time, t_0 is the pulse width, and α_2 is effective third-order NLO absorptive coefficient.

The nonlinear refractive properties of these complexes were accessed under the closed-aperture configuration while the absorptive properties under the open-aperture configuration. The valley-peak pattern of the normalized transmittance curve under the closed-aperture configuration shows characteristic self-defocusing behavior of the samples 1 and 2. The non-linear refraction of complex 3 is negligible. The effective third-order nonlinear refractive index n_2 of complexes 1 and 2 can be derived from the difference between the normalized transmittance values at the valley and peak positions ($\Delta T_v - p$) using Eq. (3) [38]

$$n_2 = \frac{\lambda \alpha_0}{0.812\pi I (1 - e^{-\alpha_0 L})} \Delta T_{\nu - p}$$
(3)

The NLO absorptive coefficients (α_2) of complexes **1–3** were calculated to be 2.201×10^{-11} , 1.467×10^{-11} and 4.991×10^{-11} mW⁻¹, respectively. From the different values between normalized transmittance at valley and peak portions, the NLO refractive index (n_2) were calculated to be -5.81×10^{-10} and -4.51×10^{-10} esu for **1** and **2**. The negative values of the third-order nonlinear refraction of complexes **1** and **2** also indicate that there are self-defocusing effects in the NLO refractive behaviors of these two bis-1,2-dithiolene complexes.

3.4. Optical limiting capabilities

It has been documented that, generally, the OL behavior of the NLO materials is affected by their NLO absorptive

Table 2

Nonlinear optical parameters of complexes 1–3 measured at 532 nm with ns laser pulses

Complex	$\alpha_2 (\mathrm{m W}^{-1})$	Im $\chi^{(3)}$ (esu)	n_2 (esu)	Re $\chi^{(3)}$ (esu)
1 2 3	$2.201 \times 10^{-11} \\ 1.467 \times 10^{-11} \\ 4.991 \times 10^{-11}$	$7.218 \times 10^{-13} 4.812 \times 10^{-13} 18.01 \times 10^{-13}$	$-5.81 \times 10^{-10} \\ -4.51 \times 10^{-10}$	$1.468 \times 10^{-13} \\ 1.142 \times 10^{-13}$



Fig. 4. Z-scan results for complex 3 (in 2.19×10^{-4} M) measured without the aperture with the ns pulses.

and refractive performances. The optical limiting effects of the three complexes were measured under nanosecond and picosecond laser pulse, respectively. Fig. 5 shows the normalized transmittance of complex 3 measured with ns and ps pulses. In order to compare the optical limiting capability conveniently, we select the same or nearly the same linear transmittance of 83%. The limiting threshold, which is defined as the incident fluence at which the transmittance fall to 50% of the corresponding linear transmittance, were summarized in Table 3. As shown in Fig. 5, the optical limiting ability of complex 3 is better than that of C₆₀ in ns measurements while it is nearly the same as that of C_{60} in ps measurements. The limiting threshold was measured as 0.12 and 0.09 J cm⁻¹ for complex 3 under ns and ps laser pulses, respectively. At the same experimental condition, the limiting thresholds of C₆₀ are determined to be 0.20 and 0.10 J cm⁻¹. Complex **3** has the capability of being more transparent than C₆₀ under laser radiation of low energies and more opaque at high energies. For the nonlinear refraction of the complexes 3 is negligible, the observed optical limiting behavior of this complex can mostly be attributed to non-linear absorptive processes. Complexes 1 and 2 display almost the same OL ability, which suggests that the counter ions have no significant effects on the third-order susceptibility $\chi^{(3)}$ and OL behavior. It is noting that the neutral complex 3 show the best OL performance in this series of compounds, which may stem from its higher oxidation state and the tight structure. For the advantages that they have highly delocalized π -systems and can exist in several clearly defined oxidation states; high thermal and photochemical stabilities; almost transparent in the visible and near-IR region (400-900 nm), these nickel-dithiolene complexes are promising candidates for optical limiting applications. The next work in our laboratory is to investigate the OL properties of those bis(dithiolene) complexes with heavier



Fig. 5. Fluence-dependent transmittance of complex **3** (in the open triangles, \triangle) and C₆₀ (in the filled block, \blacksquare) measured at 532 nm. (a) the data measured with ns laser pulses for C₆₀ (2.50×10⁻⁴M) and **3** (3.85×10⁻⁴M). (b) the data measured with ps laser pulses for C₆₀ (2.50×10⁻⁴M) and **3** (3.85×10⁻⁴M), respectively.

Table 3

The limiting thresholds of some optical limiting materials measured at 532 nm with nano- and picosecond-duration laser pulses

Compound	Solvent	Laser pulse width	Linear trans- mission (%)	Limiting threshold (J cm ⁻²)
C ₆₀	Toluene	Ns	80	0.20
(Bu ₄ N)[Ni(cddt) ₂]	DMF	Ns	85	1.0
(Ph ₄ P)[Ni(cddt) ₂]	DMF	Ns	85	1.0
[Ni(cddt) ₂]	Toluene	Ns	83	0.12
C ₆₀	Toluene	Ps	83	0.10
(Bu ₄ N)[Ni(cddt) ₂]	DMF	Ps	85	0.20
(Ph ₄ P)[Ni(cddt) ₂]	DMF	Ps	85	0.20
[Ni(cddt) ₂]	Toluene	Ps	83	0.09

metal ions. This could be one of the approaches to enhance OL ability in these compounds.

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