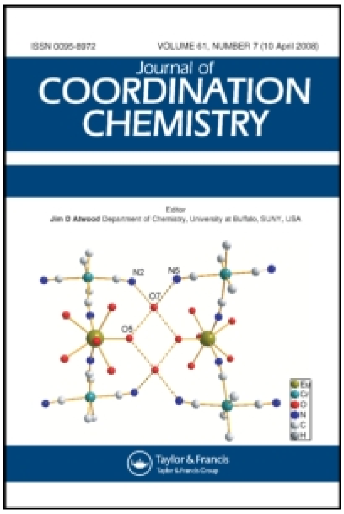

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Synthesis, structure and optical limiting properties of a new *S*-methylated derivative of a nickel dithiolene, bis[2-ethoxycarbonylsulfanyl-1,2-bis (methylthio)-1-ethenethiolato]nickel

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Synthesis, structure and optical limiting properties of a new *S*-methylated derivative of a nickel dithiolene, bis[2-ethoxycarbonylsulfanyl-1,2-bis (methylthio)-1-ethenethiolato]nickel

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The synthesis, structure and optical limiting properties of bis[2-ethoxycarbonylsulfanyl-1,2-bis (methylthio)-1-ethenetiolato]nickel, an *S*-methylated derivative of nickel dithiolenes prepared by part cleavage of 4,5-bis(methylthio)-1,3-dithiole-2-one followed by reacting with nickel salts are reported. The limiting threshold of the complex is $0.8\,\mathrm{J\,cm^{-2}}$ for 35 ps laser pulses at 532 nm which is comparable to that observed in C_{60}.

Keywords: Nickel(II); Thiolate; Structure; Optical limiting properties

1. Introduction

Optically limiting (OL) materials have been intensively studied, due to their potential applications in the protection of optical sensors and human eyes from high-intensity laser beams. Various mechanisms, including nonlinear absorption and refraction and optical excited-state absorption have been investigated [1, 2]. The most frequently reported species are fullerenes (C_{60}) [3, 4], phthalocyanine complexes [5, 6] and some inorganic clusters [7–12]. A good optical limiter should have two characteristics: (1) large transmission at low intensities followed by low transmission at high intensities, and (2) a low threshold for the onset of nonlinear attenuation of the input beam.

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Meanwhile, this ideal optical limiter should have rapid response (picoseconds for some applications) and broadband response (e.g., the visible and NIR spectrum). Because of their properties, such as electrical conductivity, super-conductivity [13–17] and third-order nonlinear optical behaviour [18, 19], nickel-dithiolenes have attracted considerable interest. More recently, the optical limiting behaviour of some nickel dithiolenes with 1,2-dithiolene ligands has been investigated as new candidates for optical limiting in the visible spectrum [20, 21–24]. As a continuation of this work, we report the syntheses, structure, and optically limiting properties of a new methylated derivative.

2. Experimental

2.1. *Chemicals*

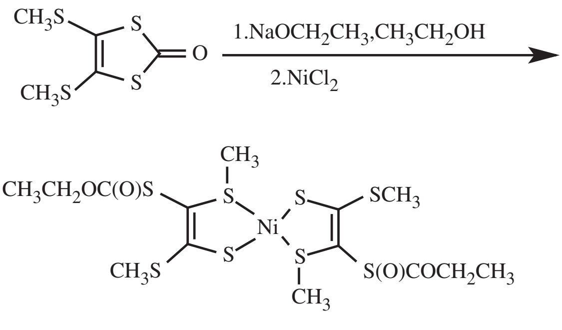
The synthetic procedure is summarized in scheme 1. 4,5-Bis(methylthio)-1,3-dithiole-2-one was prepared by literature methods [25]. All solvents were dried by standard techniques prior to use. Other chemicals used were of A.R. grade.

2.2. *Physical measurements*

Elemental analyses were performed using a Perkin–Elmer 240C instrument. IR spectra were recorded on a Nicolet FTIR 170SX spectrophotometer and electronic spectra with a Hitachi U-3410 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM-500 spectrometer. Electrospray ionization mass spectra were recorded using a Finnigan MAT SSQ 710 spectrometer.

2.3. *Synthesis*

To a slurry of 4,5-bis(methylthio)-1,3-dithiole-2-one (97 mg, 0.46 mmol) in ethanol (20 cm^3) under nitrogen, sodium ethoxide (10 cm^3, 0.01 M) was added. The mixture was stirred for 0.5 h and $NiCl_2 \cdot 6H_2O$ (55 mg, 0.23 mmol) in ethanol (10 cm^3) was added. After 1 h, a brown solid was obtained by removing the solvent under vacuum (85% yield). The complex is very stable in air and insensitive to moisture. Anal. Calcd for $C_{14}H_{22}NiO_4S_8$ (%): C, 29.70; H, 4.00. Found: C, 29.70; H, 4.00.



Scheme 1.

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{14}H_{22}NiO_4S_8$
Formula weight	569.5
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 14.609(5)$ $b = 8.562(3)$ $c = 9.729(5)$ $\beta = 90.42(5)$
Volume (Å), Z	1216.9(9), 2
Density (calculated) ($Mg\,m^{-3}$)	1.554
Absorption coefficient ($m\,m^{-3}$)	1.501
$F(000)$	588
θ range for data collection	2.8 to 25.00°
Limiting indices	$-17 \leq h \leq 17$, $-10 \leq k \leq 1$, $-1 \leq l \leq 11$
Reflections collected	2904
Independent reflections	2140 ($R_{int} = 0.025$)
Refinement method	Full-matrix least-squares on F^2
Data/restr./parameters	2140/0/175
Goodness-of-fit on F^2	0.99
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0568$, $wR_2 = 0.1147$
R indices (all data)	$R_1 = 0.0897$, $wR_2 = 0.1212$
Largest diff. peak and hole (e Å)	0.29 and −0.30

IR (KBr pellets): 1731.6 cm^{-1} ($\nu_{C=O}$). ^1H NMR d_6-acetone, ppm): 4.30 (q, 2H), 2.65 (s, 3H), 2.57 (s, 3H), 1.28 (t, 3H). Dark brown, blocky crystals were obtained by slow evaporation of a CH_3CN solution.

2.4. *X-ray crystallography*

A dark brown crystal of the complex with approximate dimensions 0.50 × 0.40 × 0.30 mm was mounted in air. Some 2904 reflections were collected on a Siemens P_4 diffractometer using ω–2θ scans. The structure was solved by direct methods and refined by full-matrix least-squares methods using 2140 observed reflections. Final R_1 and wR_2 values were 0.0568 and 0.1147, respectively. All non-H atoms were refined with anisotropic displacement parameters; H atoms were located in difference maps and included in the calculations in riding mode [26, 27]. Crystallographic data are listed in table 1 and selected bond distances and bond angles in table 2.

3. Results and discussion

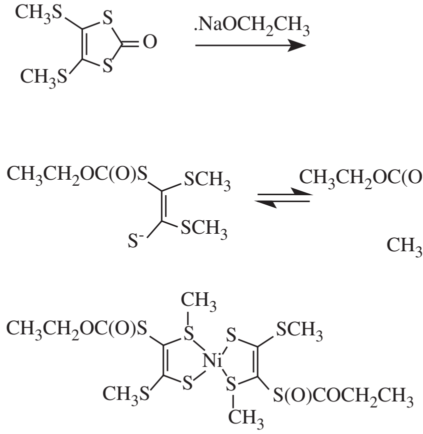
3.1. *Synthesis*

This complex was prepared by part cleavage of 4,5-bis(methylthio)-1,3-dithiole-2-one using sodium ethoxide and reaction with a nickel salt. It was identified with elemental analysis, IR and ^1H NMR. The mechanism in scheme 2 is suggested. The intermediate 2-ethoxycarbonylsulfanyl-1,2-bis(methylthio)-1-ethenethiolato anion was determined by ES MS ($m/z = 255.8$).

Table 2. Bond lengths [Å] and angles [°] for the complex.

Ni(1)–S(2)	2.1764(19)	S(2)–Ni(1)–S(1)	90.8(3)
Ni(1)–S(2)$^{\#1}$	2.1764(19)	S(2)–Ni(1)–S(1′)	88.3(9)
Ni(1)–S(1)$^{\#1}$	2.204(6)	S(2)$^{\#1}$–Ni(1)–S(1)	89.2(3)
Ni(1)–S(1)	2.204(6)	S(2)$^{\#1}$–Ni(1)–S(1′)	91.8(9)
Ni(1)–S(1′)$^{\#1}$	2.07(2)	S(1)$^{\#1}$–Ni(1)–S(1)	180.0
Ni(1)–S(1′)	2.07(2)	C(2)–S(1)–Ni(1)	102.9(5)
S(1)–C(2)	1.782(12)	C(2)–S(1′)–Ni(1)	109.6(10)
S(1)–C(1)	1.67(3)	C(1)–S(1)–Ni(1)	110.1(11)
S(1′)–C(2)	1.75(3)	C(3)–S(2)–Ni(1)	104.6(2)
S(2)–C(3)	1.743(6)	C(3)–S(3)–C(4)	104.1(3)
S(3)–C(3)	1.742(6)	C(2)–S(4)–C(5)	100.3(3)
S(3)–C(4)	1.781(6)	C(3)–C(2) –S(4)	123.9(5)
S(4)–C(2)	1.753(6)	C(3)–C(2)–S(1)	119.1(5)
S(4)–C(5)	1.787(7)	C(3)–C(2)–S(1′)	113.5(9)
O(1)–C(5)	1.183(8)	S(4)–C(2)–S(1)	116.9(4)
C(2)–C(3)	1.352(8)	S(4)–C(2)–S(1′)	120.0(7)
C(5)–O(2)	1.35(2)	C(2)–C(3)–S(2)	120.7(4)
C(5)–O(2′)	1.43(4)	C(2)–C(3)–S(3)	119.2(5)
O(2)–C(6)	1.46(4)	S(2)–C(3)–S(3)	120.0(3)
O(2′)–C(6′)	1.23(11)	O(1)–C(5)–O(2)	127.1(10)
C(7′)–C(6′)	1.44(10)	O(1)–C(5)–O(2′)	114(2)
		O(2)–C(5)–S(4)	105.8(9)
S(2)–Ni(1)–S(2)$^{\#1}$	180.0	O(2′)–C(5)–S(4)	118(2)
S(2)–Ni(1)–S(1)$^{\#1}$	89.2(3)	C(5)–O(2)–C(6)	117(2)
S(2)–Ni(1)–S(1′)$^{\#1}$	91.8(9)	C(5)–O(2′)–C(6′)	120(6)
S(2)$^{\#1}$–Ni(1)–S(1)$^{\#1}$	90.8(3)	O(2)–C(6)–C(7)	110(3)
S(2)$^{\#1}$–Ni(1)–S(1′)$^{\#1}$	88.3(9)	O(2′)–C(6′)–C(7′)	104(7)

Symmetry transformations used to generate equivalent atoms at #1: $-x, -y, -z$.



Scheme 2.

3.2. *Crystal structure*

The molecular structure and packing of the complex is shown in figure 1. The Ni atom lies at the origin and hence one half of the molecule is inversely related to the other. It is coordinated with square planar geometry with an average Ni–S bond length of 2.15 Å, which is longer than those of other nickel dithiolenes [18, 20]. The C(2)–S(1)(CH$_3$) bond length of 1.782(12) Å is consistent with a single bond and the C(3)–S(2) bond length of 1.743(6) Å is slightly longer than that of a double bond

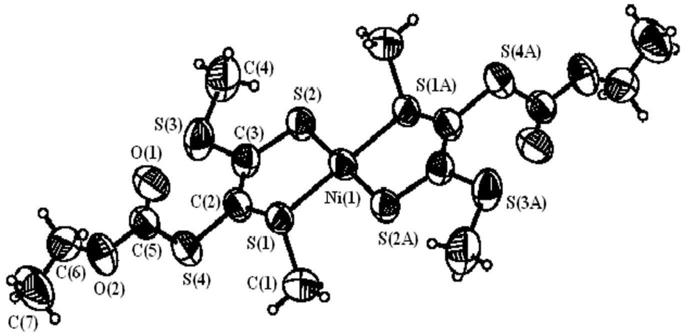


Figure 1. Molecular structure and atom labelling scheme for the complex. For clarity, the disordered SCH_3 and OCH_2CH_3 groups are depicted at single positions.

(1.71 Å), indicating a strong degree of electron delocation. The C(1)–S(1)(CH_3) and C(2)–S(1) bond lengths are longer than those of C(4)–S(3) and C(3)–S(3), respectively, due to S(1) coordinating with the Ni atom, while the bond distance between C(2) and C(3), 1.352(8) Å, is normal for a C=C bond [28]. The carboxylate groups show two different carbon–oxygen distances, 1.183(8) and 1.35(2) Å, corresponding to double and single bonds. There is no S–S contact < 3.7 Å in the crystal because of the bulky CH_3 and OCH_2CH_3 groups [29, 30, 31].

3.3. *Optical limiting properties*

In the electronic spectrum of the complex in benzene solution, the characteristic peak of multi-sulfur nickel-dithiolenes (around 1000 nm, $\varepsilon > 10\,000$) does not appear, indicating that the highly delocalized $[Ni(S_2C_2)_2]$ core is destroyed by alkylation [18, 20, 32]. It is noticed that the complex has relatively low absorption from about 500 to 1200 nm. This is important because an ideal optical limiter should be transparent at low energies.

A benzene solution of the complex was placed in a 1 mm quartz cell and irradiated by a frequency-doubled, Q-switched, mode-locked Nd : YAG laser, which produced linearly polarized 35 ps (FWHM) optical pulses at 532 nm. The laser was operated at a repetition rate of 10 Hz. Spatial profiles of the optical pulses were nearly Gaussian after passing through a spatial filter. The pulses were split into two parts: the reflected part was used as reference and the transmitted part was focused onto the sample by using a mirror of 25 cm focal length. The sample was placed at the focus where the spot radius of the pulses was measured to be 28 ± 2 mm, measured by the Z-scan technique [33]. Both the incident and transmitted laser pulses were monitored simultaneously using two energy detectors (Rjp-735 energy probes, Laser Precision). The optical limiting phenomenon was observed by measuring the nonlinear (energy-dependent) transmission. An aperture was placed in front of the transmission detector when the measurements were performed. In the experiments, the maximum incident flux at the sample was set at $4\,\mathrm{J\,cm^{-2}}$. The optical limiting effect of the complex is depicted in figure 2. At very low input flux, the optical response of the complex behaves linearly. As the incident flux reached $0.2\,\mathrm{J\,cm^{-2}}$, the transmittance began to decrease rapidly, thus exhibiting a typical optical limiting effect. We define a limiting threshold

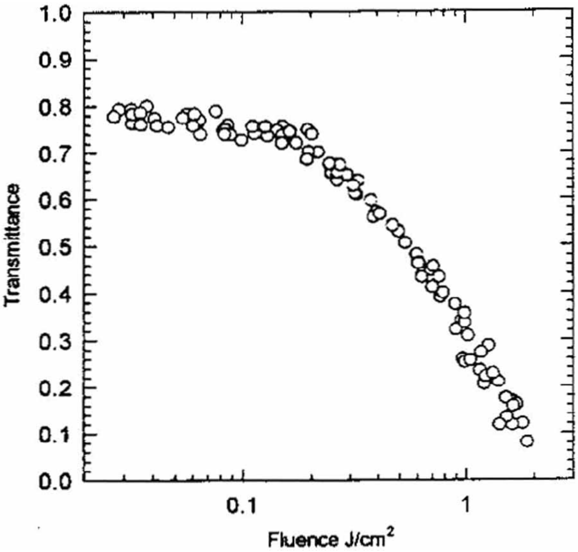


Figure 2. Optical limiting response to 35 ps 532 nm laser pulses. The complex was dissolved in benzene (5.5×10^{-4} M).

as the incident flux at which transmittance falls to 50% of the linear transmittance. The limiting threshold of the complex in benzene solution was determined to be $\sim 0.8\,\mathrm{J\,cm^{-2}}$, which is comparable to that of C_{60} in toluene solution. It should be pointed out that our measurement of the transmitted pulse energy was collected with the aperture placed at the transmission detector. Therefore, the observed limiting behaviour can be attributed to both nonlinear absorptive and refractive processes.

In addition, it is interesting to compare this new complex with the nickel complexes $[Bu_4N][Ni(bddt)_2]$ and $[Ni(bddt)_2]$ (bddt = 5,6-dihydro-5,6-butene-1,4-dithiin-2,3-dithiolate). Although the limiting threshold of the complex ($\sim 0.8\,\mathrm{J\,cm^{-2}}$) is slightly larger than those of nickel dithiolenes (~ 0.7 and $0.6\,\mathrm{J\,cm^{-2}}$) [20], it may have more broader responses due to its being almost transparent from 450 to 1400 nm. The results show that this new *S*-methylated derivative may be a new promising optical limiting material. Moreover, it indicates that it is possible to optimize optical limiting effects of nickel dithiolenes by alkylation and thus another way to new promising optical limiting materials has emerged.

Supplementary data

Crystallographic data (excluding structural factors) for the structures have been deposited in the Cambridge Crystallographic Data Centre, CCDC 255250. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (fax: +44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk).

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