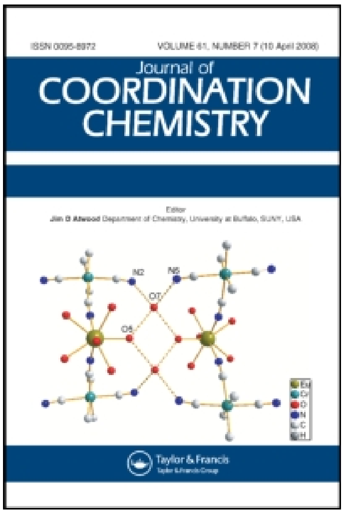

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Synthesis, crystal structure and saturable absorption in the near-IR regions of a new copper complex of dmit: hexadecyltrimethylammonium <i>bis</i>(2-thioxo-1,3-dithiole-4,5-dithiolato)-copper

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Synthesis, crystal structure and saturable absorption in the near-IR regions of a new copper complex of dmit: hexadecyl-trimethylammonium *bis*(2-thioxo-1,3-dithiole-4,5-dithiolato)-copper

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A new copper complex of dmit, hexadecyltrimethylammonium *bis*(2-thioxo-1,3-dithiole-4,5-dithiolato)-copper($[C_{16}H_{33}(CH_3)_3N][Cu(dmit)_2]$, abbreviated as CTCU, $C_{16}H_{33}(CH_3)_3N =$ hexadecyltrimethylammonium, dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) has been synthesized and its structure determined by X-ray diffraction. The saturable absorption of CTCU at 1053 nm shows promise as a Q-switch dye in the near IR regions.

Keywords: Saturable absorption; Copper-dmit salt; Q-switching; Crystal structure

1. Introduction

Transition metal *bis*-dithiolene complexes have attracted attention due to their potential applications as electrical conductors and superconductors, and optical and photo-electrical materials [1–3]. It has been reported that nickel dithienes are particularly suitable for Q-switching lasers in the near infrared region [4, 5].

Some copper complexes of dmit have been reported [6–12], most as 2 : 1 type salts of $[Cu(dmit)_2]^{2-}$. To our knowledge, only one 1 : 1 type salt of $[Cu(dmit)_2]^{-}$ has been reported which was prepared for thin film gas sensor applications using electrodeposition [7]. Here, we report the synthesis, characterization, crystal structure and the third-order optical response of a new 1 : 1 type copper-dithiolene complex, hexadecyltrimethylammonium *bis*(2-thioxo-1,3-dithiole-4,5-dithiolato)-copper

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($[C_{16}H_{33}(CH_3)_3N]^+[Cu(dmit)_2]^-$, abbreviated as CTCU). For the first time a 1 : 1 type copper complex of dmit has been prepared and its crystal structure determined. The third-order optical nonlinearities of its acetone solution are investigated using *Z*-scan method with 1 ns pulse width at 1053 nm.

2. Experimental

All chemicals were of reagent grade obtained from commercial sources and used without further purification. Dmit ($(COC(CH_3)_3)_2$) was prepared according to the procedure reported previously [13].

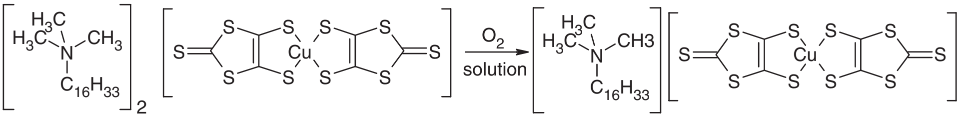
Elemental analyses were carried out using a Pekin-Elmer 2400 instrument. The linear absorption spectrum was recorded using a Hitachi U-3500 UV-Vis-NIR scanning spectrophotometer.

Preparation procedure is a modification according to literature method [14]. Dmit ($(COC(CH_3)_3)_2$) (0.732 g, 2 mmol) was treated with an excess of sodium methylate (0.5 M) in MeOH (20 mL) under nitrogen at room temperature with stirring. To the resulting purple solution was added dropwise $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) in MeOH (20 mL). After 15 min, the solution was stirred in air for 1 h and then cetyltrimethylammonium bromide (CTAB) (0.874 g, 2.4 mmol) in MeOH (20 mL) was added. The resulting precipitate was washed with MeOH. The precipitation was a 2 : 1 type salt, i.e. the anion was $[Cu(dmit)_2]^{2-}$. The crystals used for the X-ray structure determination were obtained by slow recrystallization from acetone. During recrystallization in acetone solution, oxidization by oxygen dissolved, occurred as shown in scheme 1. Therefore, the final crystals obtained from solution were the 1 : 1 type salt of $[Cu(dmit)_2]^-$. The oxidation reaction occurred by losing one of the electrons of the π-conjugated system, i.e. the whole anion moiety. Anal. Calcd for $C_{25}H_{42}NS_{10}$(%): C, 40.53; H, 5.72; N, 1.89; S, 43.28;%. Found: C, 40.81; H, 6.13; N, 2.04; S, 43.17.

A brown block crystal of CTCU with approximate dimensions $0.27 \times 0.22 \times 0.18\,\mathrm{mm}^3$ was mounted in air. The intensity data were collected at 293(2) K on a Bruker P4 diffractometer and Mo-Kα radiation ($\lambda = 0.071069$ nm) was used. By using SHELXTL-97 programs [15], the structure was solved by direct methods and refined by full-matrix least-squares on F^2, with 4036 unique, absorption corrected ($T_{\min} = 0.75$, $T_{\max} = 0.80$), reflections. All non-hydrogen atoms were anisotropocally refined. The refinement converged at $R = 0.0517$, $\omega R = 0.109$ for a total of 335 parameters and 4036 observed reflections with $[I > 2.0\sigma(I)]$. Table 1 lists the crystallographic data.

Atomic coordinates for all the non-hydrogen atoms are listed in table 2, and selected atomic distances and bond angles are listed in table 3.

The third-order nonlinear properties of an acetone solution of complex ($1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) were measured by *Z*-scan technique [16, 17]. The laser beam was



Scheme 1. Oxidation and formation of CTCU in solution.

Table 1. Crystal data and structure refinement for CTCU.

Chemical formula	$C_{25}H_{42}NS_{10}Cu$
Formula weight	740.74
Crystal system	Triclinic
Space group	$P\bar{1}$
μ (mm^{-1})	1.241
Calculated density ($mg\,m^{-3}$)	1.409
Unit cell dimensions (Å, °)	
a	8.0364(10)
b	12.2621(9)
c	18.3518(15)
α	93.386(6)
β	99.348(9)
γ	100.612(8)
V(Å^3)	1746.5(3)
Z	2
T (K)	293(2)
Measured/independent reflections (R_{int})	8826/7223(0.0281)
R	0.0517

generated from a Q-switched Nd : YLF laser with a laser pulse width of 1ns operating at the repetition rate of 1 Hz at 1053 nm wavelength. The sample is moved along the optic axis (the z-direction) through the focus of the lens, which has a focal length of 150 mm, while the energy transmitted through an aperture in the far field is recorded as a function of the sample position. The reference beam energy and the on-axis transmitted beam energy through an open-aperture (OA) were measured by an energy ratiometer simultaneously. The radius of the beam waist (w_0) was 30.8 µm. The Rayleigh length, z_0, was calculated to be 2.84 mm, longer than the thickness of a quartz cell with the optical length of 1 mm containing the sample. Before measuring this sample the system was calibrated using CS_2 as reference. Measurement on pure acetone was also performed under the same measuring conditions, showing that the Z-scan curves originated from the sample, CTCU, not from the solvent or the quartz cuvette.

3. Results and discussion

The X-ray crystal structure determination of CTCU (figure 1) shows that the Cu atom is coordinated in a slightly distorted square-planar geometry with the two vicinal exocyclic sulfur atoms of the two chelating ligands. The two five-membered rings containing metal atom are virtually planar with a maximum deviation of 0.075(1) Å for C2 and 0.023 Å for C4. As shown in table 3, all C–S bond lengths in the circles are shorter than that of a C–S single bond (1.82 Å) [18] and similar to those found previously in four-coordinate copper(II) complexes [17, 19–21]. The Cu–S bond lengths, with an average of 2.1572 Å, are shorter than those of 2 : 1 type complexes such as $[Cu(mnt)_2]^{2-}$ (mnt = maleonitriledithiolate) and $[Cu(dmit)_2]^{2-}$ [22–24], which indicates stronger interaction between the metal ion and the organic ligand. The S–Cu–S bond angles for the vicinal S atoms, ranging from 87.03(5) to 92.92(4)°, are close to the normal right angle. The other two S–Cu–S bond angles of 176.43(6), 174.91(6)° are close to 180°. The geometry around copper is nearly planar, with a dihedral angle of

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for CTCU. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

U_{eq}	x	y	z	$10^3 U_{eq}/\text{Å}^2$
C(1)	3004(6)	1299(3)	5284(3)	70(1)
C(2)	3392(5)	2946(3)	4455(2)	54(1)
C(3)	2679(5)	3318(3)	5022(2)	53(1)
C(4)	3255(5)	7199(3)	3131(2)	57(1)
C(5)	2397(5)	7531(3)	3647(2)	52(1)
C(6)	2645(5)	9129(3)	2782(2)	60(1)
C(7)	6982(10)	17204(5)	−1243(4)	147(3)
C(8)	7531(10)	16134(5)	−1253(4)	137(3)
C(9)	7018(9)	15355(4)	−721(3)	109(2)
C(10)	7548(9)	14273(4)	−731(3)	114(2)
C(11)	7107(8)	13501(4)	−190(3)	103(2)
C(12)	7662(8)	12414(4)	−211(3)	103(2)
C(13)	7302(8)	11671(4)	368(3)	100(2)
C(14)	7857(8)	10585(4)	356(3)	96(2)
C(15)	7514(8)	9867(4)	951(3)	96(2)
C(16)	8139(7)	8809(4)	973(3)	89(2)
C(17)	7774(7)	8093(4)	1573(3)	93(2)
C(18)	8422(7)	7049(4)	1593(3)	85(2)
C(19)	7983(7)	6272(4)	2161(3)	85(2)
C(20)	8624(7)	5241(4)	2156(3)	85(2)
C(21)	8076(7)	4406(4)	2674(3)	76(1)
C(22)	8915(7)	3415(4)	2640(3)	77(1)
C(23)	6507(6)	1897(4)	2736(3)	74(1)
C(24)	8390(6)	2827(4)	3853(2)	73(1)
C(25)	9467(6)	1658(4)	3002(3)	90(2)
N(1)	8291(4)	2473(3)	3059(2)	55(1)
S(1)	2988(2)	99(1)	5637(1)	109(1)
S(2)	3771(2)	1594(1)	4478(1)	74(1)
S(3)	2252(2)	2380(1)	5675(1)	72(1)
S(4)	3830(2)	3755(1)	3756(1)	65(1)
S(5)	2225(2)	4630(1)	5070(1)	59(1)
S(6)	3853(2)	5926(1)	3114(1)	71(1)
S(7)	1881(2)	6687(1)	4324(1)	67(1)
S(8)	3660(2)	8134(1)	2471(1)	79(1)
S(9)	1818(2)	8823(1)	3571(1)	69(1)
S(10)	2492(2)	10274(1)	2365(1)	84(1)
Cu(1)	2962(1)	5256(1)	4071(1)	54(1)

7.09(17)° between the two dmit planes. The copper atom deviates by 0.095(1) and 0.070(1) Å from each dmit plane, respectively. The CuS_4 core adopts a slightly distorted square-planar conformation. Therefore, the $[Cu(dmit)_2]^-$ monoanion exhibits planar geometry.

A packing diagram viewed along the *c*-axis is shown in figure 2. The closest intermolecular S $\cdots$ S contact is 3.641(2) Å, equal to the sum of van der Waals radii of two S atoms. Therefore, the intermolecular interaction is weak.

The UV-Vis-NIR spectrum CTCU in 10^{-4} M acetonitrile solutions (figure 3) shows five absorptions at 315, 393, 443, 617 and 1027 nm, respectively. The two peaks at 315 and 393 nm are assigned to local excitation of the dmit ligand and the peak at 443 nm is assigned to Cu $\leftarrow$ S charge transfer (c.t.) transition (d–p interaction) [12]. The peak at 617 nm corresponding to the d–d transition is quite weak. The strong broad absorption at 1027 nm is ascribed to a π–π^* transition ($2b_{1u} \rightarrow 3b_{2g}$) between the HOMO and the LUMO, which is similar to those of nickel complexes ($[Ni(Pr^i timdt)_2]^-$, $[Ni(dmit)_2]^-$,

Table 3. Selected bond lengths (Å) and angles (°) for CTCU.

S(4)–Cu(1)	2.1644(11)
S(5)–Cu(1)	2.1570(12)
S(6)–Cu(1)	2.1517(12)
S(7)–Cu(1)	2.1557(11)
C(1)–S(1)	1.640(4)
C(1)–S(3)	1.721(4)
C(1)–S(2)	1.724(5)
C(2)–C(3)	1.362(5)
C(2)–S(4)	1.710(4)
C(2)–S(2)	1.741(4)
C(3)–S(5)	1.714(4)
C(3)–S(3)	1.740(4)
C(4)–C(5)	1.345(5)
C(4)–S(6)	1.715(4)
C(4)–S(8)	1.746(4)
C(5)–S(7)	1.717(4)
C(5)–S(9)	1.739(4)
C(6)–S(10)	1.654(4)
C(6)–S(8)	1.707(4)
C(6)–S(9)	1.721(4)
C(1)–S(2)–C(2)	97.4(2)
C(1)–S(3)–C(3)	97.5(2)
C(2)–S(4)–Cu(1)	102.05(14)
C(3)–S(5)–Cu(1)	102.32(15)
C(4)–S(6)–Cu(1)	102.06(15)
C(5)–S(7)–Cu(1)	102.57(14)
C(6)–S(8)–C(4)	97.7(2)
C(6)–S(9)–C(5)	97.1(2)
S(6)–Cu(1)–S(7)	92.92(4)
S(6)–Cu(1)–S(5)	176.43(6)
S(7)–Cu(1)–S(5)	87.25(4)
S(6)–Cu(1)–S(4)	87.03(5)
S(7)–Cu(1)–S(4)	174.91(6)
S(5)–Cu(1)–S(4)	93.12(4)

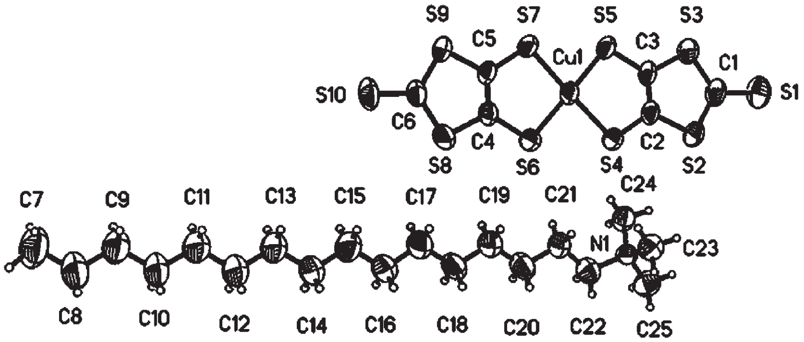


Figure 1. The molecular structure of CTCU, showing 50% probability displacement ellipsoids.

and $[Ni(bddt)_2]^-$ displaying strong absorption at 1400 (in THF), 1130 (in THF), and 1180 nm (in acetonitrile), respectively) [4, 25, 26]. The low-energy transition in the NIR regions makes it possible for CTCU to be a NIR dye in Q-switching neodymium lasers, which operate at 1064 nm.

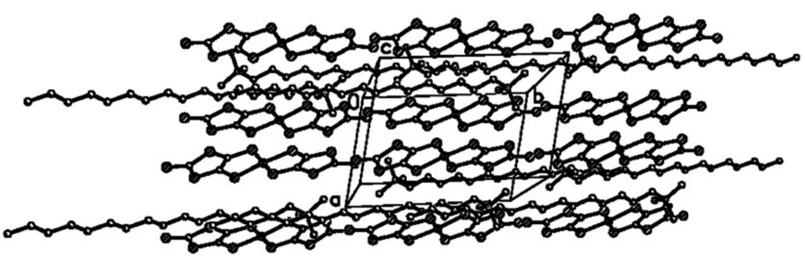


Figure 2. Packing diagram for the title compound viewed along the *c*-axis. H atoms have been omitted for clarity.

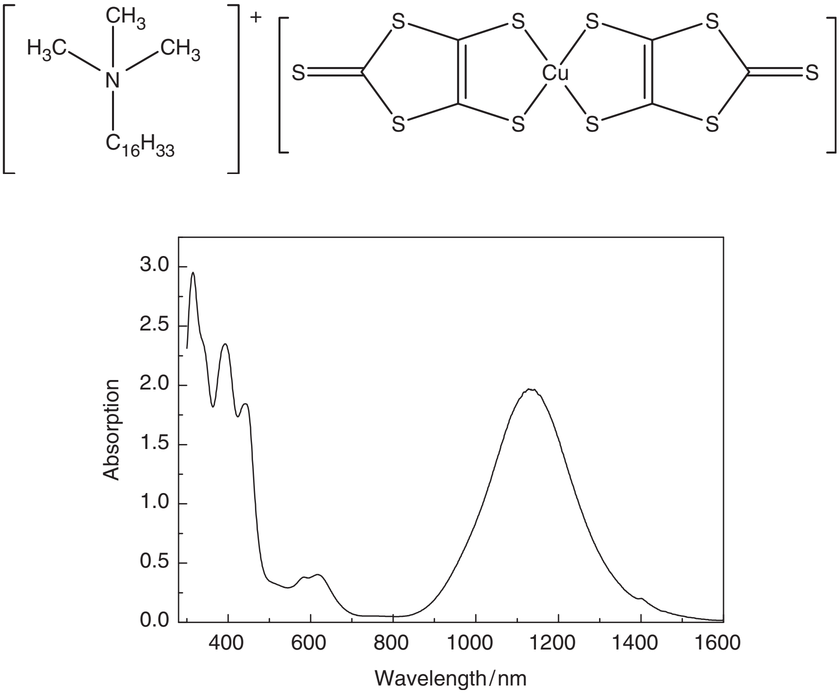


Figure 3. Molecular structure and absorption spectrum of CTCU in acetonitrile (10^{-4} M).

Figure 4 exhibits the OA curve recorded by the *Z*-scan technique. The nonlinear absorption coefficient β ($\mathrm{m\,W^{-1}}$), defined as

$$\alpha = \alpha_0 + \beta I \tag{1}$$

can be calculated using the equation (2) [27]:

$$T(z, S=1) = \sum_{m=0}^{\infty} \frac{[-\beta I_0 L_{\mathrm{eff}}/(1 + z^2/z_0^2)]^m}{(m+1)^{3/2}} \tag{2}$$

where $T(S=1)$ is the normalized transmittance for the open-aperture, $L_{\mathrm{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample (L is the sample

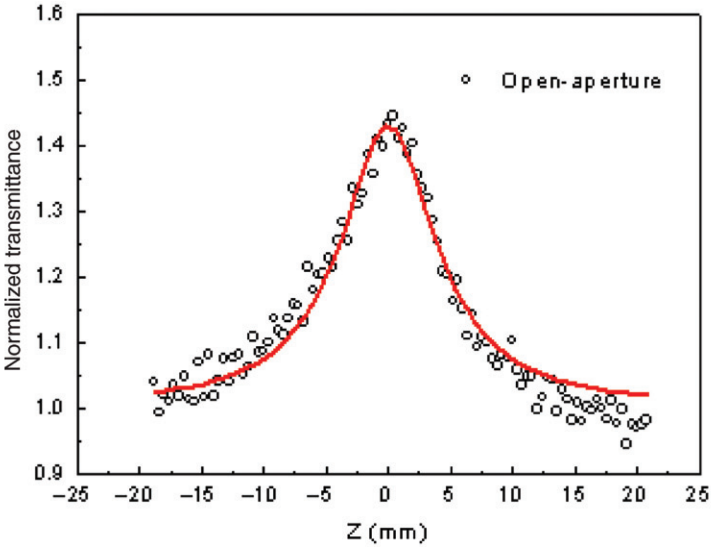


Figure 4. Z-scan transmittance curves of sample in acetone (10^{-4} M). Solid line shows theoretical fit.

thickness), α_0, the linear absorption coefficient of the sample, is $3.21\,\mathrm{cm}^{-1}$ at 1053 nm, and $I_0 = 9.7\,\mathrm{GW\,cm}^{-2}$, is the laser intensity at the focal point. Theoretical fit of the experimental data could be conducted by substitution of equation (1) into equation (2). The solid line in figure 4 shows the theoretical fit which is in good agreement with the experimental results, indicating that the model used is reasonable.

The OA curve exhibits saturable absorption property of the sample. The nonlinear absorption β is measured to be $1.47 \times 10^{-11}\,\mathrm{m\,W}^{-1}$.

Some compounds show strong linear absorption in the near-IR regions. However, not all of them possess saturable absorption, making them unsuitable for laser pulse compression. As early as 1975, Reynolds *et al.* reported that monoanions of Ni-dithiene complexes did not produce Q-switching; neutral complexes of analogs did produce Q-switching although their absorption spectra were similar [5]. In fact, they reported that none of a series of monoanions of nickel complexes could cause Q-switching. However, the saturable absorption at 1053 nm of CTCU makes CTCU a potential candidate as a near-IR dye in Q-switching neodymium lasers.

4. Conclusions

A new 1 : 1 type copper complex of dmit, CTCU, has been synthesized and characterized. The NLO properties of its acetone solution with a concentration of $10^{-4}\,\mathrm{mol\,L}^{-1}$ are investigated by the Z-scan technique at 1053 nm with 1 ns laser duration. The nonlinear absorption coefficient β is $1.47 \times 10^{-11}\,\mathrm{m\,W}^{-1}$. CTCU may be a potential material as near-IR dye in Q-switching neodymium lasers for its saturable absorption at 1053 nm.

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