Synthesis, Crystal Structure and Third-Order Nonlinear Optical Behavior of a Novel Dimeric Mixed-Ligand Zinc(II) Complex of 1,3-Dithiole-2-thione-4,5-dithiolate

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The first dimeric mixed-ligand zinc(II) complex of 1,3-dithiole-2-thione-4,5-dithiolate (dmit) [Zn(dmit)(2,2′-bpy)]$_2$ (2,2′-bpy = 2,2′-bipyridine) (**1**), which exhibits a good third-order nonlinear refraction effect, was synthesized by a ligand exchange reaction between [$(Et_4N)_2$Zn(dmit)$_2$] and [Cu(2,2′-bpy)$(NO_3)_2$]·$2H_2O$. A Z-scanning measurement of complex **1** gives the third-order nonlinear refraction index $n_2 = 3.72 \times 10^{-18}$ m^2/W and the real part $\mathrm{Re}\chi^{(3)} = 1.01 \times 10^{-12}$ esu. Crystal data for **1**: monoclinic, $P2_1/c$ (No.14), a = 11.556(2) Å, b = 9.141(2) Å, c = 15.020(3) Å, β = 109.55(3)°, Z = 4.

Introduction

Metal bis-dithiolene complexes have aroused more and more interest over the past decades due to their potential applications as precursors for electrical conductors and superconductors;[1] the optical properties of these compounds are also very interesting. For example, in 1972 Drexhage and co-workers discovered that transition metal dithiolene complexes are very stable to intense irradiation in the near-infrared region and are particularly suitable for Q-switching lasers.[2,3] Recently, more and more symmetrical bis-dithiolene complexes with third-order optical nonlinearity or optical limiting effects have been explored.[4] Because of the large values of their third-order nonlinear susceptibility $\chi^{(3)}$ [1a,5] and negative molecular first hyperpolarizability(β),[1a,6] unsymmetrical dithiolene complexes have also become promising candidates for nonlinear optical materials. Herein we report the synthesis, crystal structure and third-order nonlinear optical behavior of a novel dimeric mixed-ligand zinc(II) complex of 1,3-dithiole-2-thione-4,5-dithiolate (dmit) [Zn(dmit)(2,2′-bpy)]$_2$ (**1**). To the best of our knowledge, this is the first example of a dimeric mixed-ligand complex of dmit.

Results and Discussion

[$(Et_4N)_2$Zn(dmit)$_2$] and [Cu(2,2′-bpy)$(NO_3)_2$]·$2H_2O$ were successfully employed for the preparation of complex **1**. This result illustrates that even complexes with different metal ions can be utilized for ligand-exchange reactions with transition metal dithiolene complexes.[1a,7] As we know, the metal ions are usually the same when a ligand exchange reaction, which takes place between symmetrical metal bischelate of dmit and that of the other ligand,[7c,7d] was used.

In the IR spectra of **1** the C=S and S−C−S stretching bands of the dmit ligand show no significant differences from the symmetrical dmit complexes.[1,8] The electronic spectrum of **1** in DMF exhibits two bands in the 270−700 nm region: the sharp band at 286 nm is assigned to a π-π* transition and the broad band at 497 nm to an n-π* transition of the dmit ligand. Both bands show blue shifts relative to those in [Na_2(dmit)] (316, 514 nm in MeOH),[9] [NBu_4]$_2$[Zn(dmit)$_2$] (300, 530 nm in MeCN)[9] and [NMe_4]$_2$[Zn(dmit)(Sph)$_2$] (327, 512 nm).[1a]

The crystal structure of **1** consists of discrete neutral dmit complex dimers [Zn(dmit)(2,2′-bpy)]$_2$. As shown in Figure 1, each zinc atom is coordinated in a distorted square-pyramidal geometry, with two nitrogen atoms from the 2,2′-bipyridine ligand and two sulfur atoms from one dmit ligand forming the base of the pyramid and one sulfur from the other dmit ligand occupying the apical site. One of the two sulfur atoms in each dmit ligand therefore acts as a μ_2-bridge to link two zinc atoms; a similar μ_2-S bridging mode of dmit was also observed in the symmetrical dmit complexes [NnBu$_4$][Fe$(C_3S_5)_2$] and [Fe$(C_5Me_5)_2$][Fe$(C_3S_5)_2$].[10]

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The Zn−N and Zn−S bond lengths [average 2.136(2) and 2.4424(9) Å, respectively] are a little longer than those in another dimeric zinc complex [Zn_2(*i*-MNT)$_2$(4-mpy)$_4$]·$CHCl_3$ (*i*-MNT = isomaleonitrile dithiolate) [average 2.056(4) and 2.319(1) Å, respectively].[11] The Zn−Zn distance (3.357 Å) is also a little longer than the Fe−Fe distances in [N*n*Bu_4][Fe(C_3S_5)$_2$] (3.17 Å) and [Fe(C_5Me_5)$_2$][Fe(C_3S_5)$_2$] (3.169 and 3.164 Å).[10] It is noteworthy that complex **1** is, to the best of our knowledge, the first dimeric mixed-ligand complex with dmit, although dimers with metal-sulfur bonds in symmetrical bis-dithiolene complexes are common.[12]

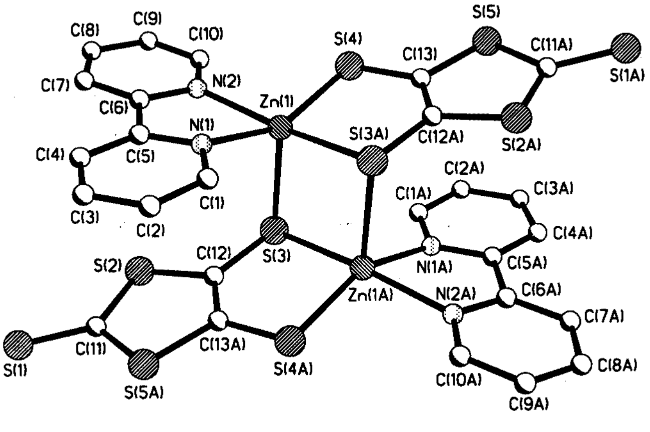

Figure 1. Molecular structure of complex **1**; selected bond lengths (Å) and angles (°): Zn(1)−N(1) 2.104(2), Zn(1)−N(2) 2.168(2), Zn(1)−S(4) 2.3374(8), Zn(1)−S(3) 2.4902(9), Zn(1)−S(3A) 2.4995(11); N(1)−Zn(1)−N(2) 76.06(8), S(3A)−Zn(1)−S(4) 91.18(3), N(2)−Zn(1)−S(4) 93.80(7), N(1)−Zn(1)−S(3A) 94.04(6), N(1)−Zn(1)−S(3) 97.26(6), N(2)−Zn(1)−S(3) 95.57(6), S(4)−Zn(1)−S(3) 106.94(3), S(3A) −Zn(1)−S(3) 95.42(3)

Another interesting structural feature is the molecular arrangement of the [Zn(dmit)(2,2′-bpy)]$_2$ dimers (Figure 2). Unlike other metal bis-dithiolene dimers,[10,12] the [Zn(dmit)(2,2′-bpy)]$_2$ dimers link each other through short S···Zn contacts rather than through short S···S contacts. These S···Zn contacts (3.676 Å) also suggest that there are π-π stacking interactions among dmit groups rather than 2,2′-bipyridine ligands from neighboring [Zn(dmit)(2,2′-bpy)]$_2$ dimers. The center-to-center distance between the C_3S_2 five-membered rings of two adjacent dmit groups is 3.745 Å. Therefore, discrete [Zn(dmit)(2,2′-bpy)]$_2$ dimers are further extended into an interesting one-dimensional supermolecular array by π-π stacking interactions between dmit groups.

Complex **1** crystallizes in the centrosymmetric space group $P2_1/c$, which cannot meet the essential requirement of electronic asymmetry for second-order nonlinear optical (NLO) effects.[13] However, complex **1** does possess third-order nonlinear optical behaviour. The third-order optical nonlinearity of complex **1** was determined by using the *Z*-scan technique.[14−16] These results are shown in Figure 3, where the filled and open circles were measured with and without the aperture, respectively. The valley/peak pattern of the normalized transmittance shows a characteristic self-focusing behavior of the propagating light in the sample.

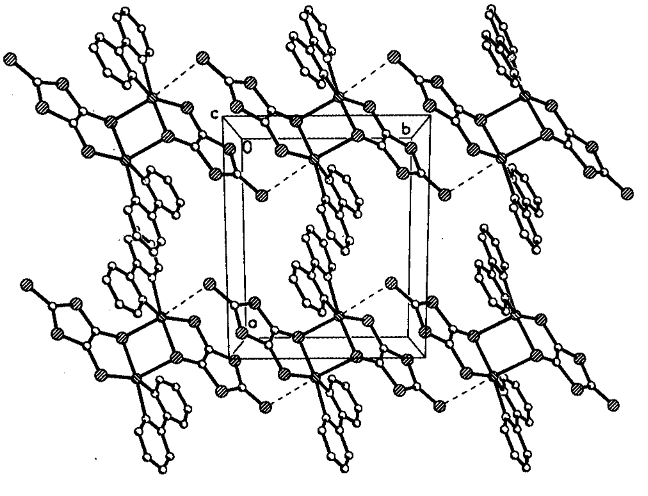

Figure 2. A packing diagram of the unit cell of complex **1** looking down the *c* axis showing how the discrete [Zn(dmit)(2,2′-bpy)]$_2$ dimers are further extended into interesting one-dimensional supermolecular arrays through short S···Zn contacts or π-π stacking interactions between dmit groups

According to the method described in literature,[14−16] the value of the third-order nonlinear refraction index n_2 is calculated to be 3.72×10^{-18} m^2/W and the real part of the third-order nonlinear susceptibility Re$\chi^{(3)}$ to be 1.01×10^{-12} esu. The value of Re$\chi^{(3)}$ of **1** is similar to other promising NLO media such as phthalocyanine, porphyrin and pentaazadentate and stilbazolium derivatives,[15] indicating that complex **1** is a good candidate for a nonlinear optical material.

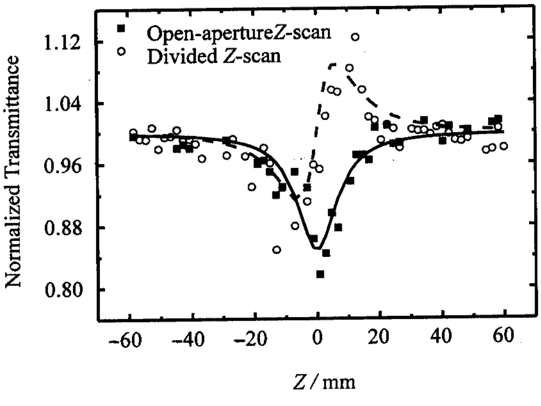

Figure 3. *Z*-scan measurement of complex **1** in a 4.05×10^{-5} mol·dm^{-3} solution of DMF at 532 nm with I_0 = 0.6 GW/cm^2; the data collected under the closed-aperture configuration show the self-focusing effect

In conclusion, an interesting dimeric mixed-ligand zinc(II) complex of dmit [Zn(dmit)(2,2′-bpy)]$_2$, which exhibits good third-order nonlinear refraction effect, was synthesized by a ligand-exchange reaction between [Et_4N]$_2$[Zn(dmit)$_2$] and [Cu(2,2′-bpy)(NO_3)$_2$]·$2H_2O$. This demonstrates that the ligand-exchange reaction method for preparing mixed-ligand complexes of dmit is also feasible when the metal ions of the two reactants are different.

Experimental Section

All reagents were obtained from commercial sources and used without further purification. The elemental analyses were performed on a Heraeus Chn-Rapid elemental analyzer. The infrared spectra were recorded on a Perkin−Elmer 2000 spectrophotometer with pressed KBr pellets. Bis(tetraethylammonium) bis(1,3-dithiole-2-thione-4,5-dimercapto)zincate {$[Et_4N]_2[Zn(dmit)_2]$} was prepared according to the literature method.[8]

Synthesis of 1: Single crystals were grown in a test tube. Solid $[Cu(2,2'\text{-bpy})(NO_3)_2]\cdot 2H_2O$ (0.2 mmol) was dissolved in 3 mL of water and 5 mL of MeOH, and to this solution was added carefully a solution of $[Et_4N]_2[Zn(dmit)_2]$ (0.2 mmol) in Me_2CO (10 mL). The test tube was then allowed to stand undisturbed at room temperature for three days, yielding a dark red block of **1** on the tube wall (8.4 mg, ca. 20% yield based on Zn) together with some unknown black amorphous materials at the bottom. $C_{26}H_{16}N_4S_{10}Zn_2$ (835.8): calcd. C 37.37, H 1.93, N 6.70; found C 37.29, H 1.98, N 6.62. IR (KBr): $\tilde{\nu}$ = 1595(m), 1566(w), 1489(w), 1472(m), 1440(s), 1429(s), 1315(m), 1249(w), 1171(w), 1158(w), 1059(s), 1031(vs), 891(m), 765(s), 733(m), 652(w), 629(w), 529(w), 465(m), 415(w) cm^{-1}. UV (1×10^{-4} M DMF): λ_{max} = 286 nm ($\varepsilon = 3.73 \times 10^4$ $M^{-1}cm^{-1}$), 497 nm ($\varepsilon = 1.49 \times 10^4$ $M^{-1}cm^{-1}$). ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 8.73 (br, 1 H, Hpy), 8.43 (br, 1 H, Hpy), 8.02(br, 1 H, Hpy), 7.52 (br, 1 H, Hpy) ppm.

Crystallographic Analysis: A dark-red single crystal with dimensions of 0.2 × 0.1 × 0.1 mm was mounted on a Bruker SMART CCD diffractometer equipped with Mo-K_α radiation (λ = 0.71073 Å) at room temperature and data were collected with the ω-scan technique. Cell parameters were obtained by the global refinement of the positions of all collected reflections. A total of 13737 data of which 5504 independent reflections (R_{int} = 0.0417) were collected in the range of $5.30° \le 2\theta \le 66.92°$($-15 \le h \le 17$, $-13 \le k \le 12$, $-22 \le l \le 22$), and 3043 with $I > 2\sigma(I)$ were used in the refinement of the structure. The data were corrected for Lorentz-polarization effects during data reduction using XSCANS.[17a] Empirical absorption corrections based on Ψ-scan measurements were applied ($T_{min,max}$: 0.759012, 1.000000).

Table 1. Crystal data for complex **1**

	1
Chemical formula	$C_{13}H_8N_2S_5Zn$
Fw	417.88
Space group	$P2_1/c$ (No. 14)
a, Å	11.556(2)
b, Å	9.141(2)
c, Å	15.020(3)
α, deg	90
β, deg	109.55(3)
γ, deg	90
V, Å^3	1495.1(5)
Z	4
D_c, g cm^{-3}	1.856
μ (Mo-K_α), mm^{-1}	2.331
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0452, 0.0583

[a] $R_1 = ||F_o| - |F_c||/|F_o|$, $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL-97 program.[17b] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were treated as riding atoms. Selected crystallographic data and structure determination parameters for complex **1** are given in Table 1.

CCDC-176197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Non-Linear Optical Measurements: The NLO properties of a solution of **1** in DMF were determined by using a standard Z-scan setup with a Q-switched, frequency-doubled Nd:YAG laser.[18] The pulse-repetition rate was 10 Hz. The transmittance of the aperture in front of the detector for a closed-aperture measurement was 0.1. The solution was contained in a 2 mm thick quartz cell.

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