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A New Method to Synthesize Unsymmetrical Dithiolene Metal Complexes of 1,3-Dithiole-2-thione-4,5-dithiolate for Third-Order Nonlinear Optical Applications

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Interest in metal bis-dithiolenes has increased over the past decades since they have been intensively studied as materials for electrical conductors.[1] These compounds are also found to exhibit unusual optical properties. They are known to be very stable to intense irradiation in the near-infrared region and have been used as Q-switch dyes for Nd:YAG lasers.[2] A series of symmetrical complexes with third-order optical nonlinearity were reported and were considered to be promising candidates for all-optical signal-processing devices.[3] Recently, large values of third-order nonlinear susceptibility $\chi^{(3)}$[4] as well as negative molecular first hyperpolarizability (β)[5] were observed for some unsymmetrical dithiolene−metal complexes. It is therefore attractive to explore the synthesis of unsymmetrical dithiolene complexes and to study their nonlinear optical (NLO) properties.

Up to now, there have been two useful methods for the synthesis of mixed ligand complexes with 1,3-dithiole-2-thione-4,5-dithiolate (dmit) (Scheme 1). One is a conventional metathesis reaction of the dmit dianion with the corresponding dichloro−metal complexes, method 1. The other is a ligand exchange reaction, which is a reaction between two symmetrical metal bis-chelates of dmit and the other ligand, method 2.

The direct method 1 is very conventional in the synthesis of neutral complexes from neutral dichloro compounds. For instance, [Pt(phen)(dmit)] has been prepared from [Pt(phen)Cl$_2$],[6] and [W(Cp)$_2$(dmit)] has been prepared from [W(Cp)$_2$ Cl$_2$][7] (phen = 1,10-phenanthroline, Cp = η-C$_5$H$_5$). However, mixed ligand anions with dichloride are not always easy to prepare. For these dmit mixed complexes, the most efficient method is a ligand exchange reaction 2. For example, [Zn(dmit)(Et$_2$dtc)]$^-$ was prepared by reaction of [Zn(dmit)$_2$]$^{2-}$ with [Zn(Et$_2$dtc)$_2$],[8] and [Ni(dsit)(i-mnt)]$^{2-}$ has been prepared from [Ni(dsit)$_2$]$^{2-}$ and [Ni(i-mnt)$_2$]$^{2-}$[9] (Et$_2$dtc = diethyl-dithiocarbamate, i-mnt = 1,1-dicyanoethene-2,2-dithiolate, C$_4$N$_2$S$_2$$^{2-}$, and dsit = 2-thione-1,3-dithiole-4,5-diselenolate, C$_3$Se$_2$S$_3$$^{2-}$). During our work on the syntheses of mixed ligand complexes, however, we found in some cases that the ligand exchange reaction was not always complete and that separation of the reaction mixture was not easy.

Scheme 1

$$\text{(1)}\quad (\mathrm{dmit})^{2-} + [\mathrm{M(LL)Cl_2}] \longrightarrow [\mathrm{M(dmit)(LL)}] + 2\,\mathrm{Cl}^-$$

$$\text{(2)}\quad [\mathrm{M(dmit)_2}]^{2-} + [\mathrm{M(LL)_2}]^{2-} \longrightarrow 2\,[\mathrm{M(dmit)(LL)}]^{2-}$$

Herein we report a new method to synthesize unsymmetrical dithiolene metal complexes such as (Me$_4$N)$_2$[Cd(dmit)(Sph)$_2$] (**1**)[10] and (Me$_4$N)$_2$[Zn(dmit)(Sph)$_2$] (**2**)[11] (Sph = thiophenolate group). The method we used is called the cluster-cracking reaction 3.

$$(3)4\,(\mathrm{dmit})^{2-} + [\mathrm{M_4(Sph)_{10}}]^{2-} \rightarrow 4[\mathrm{M(dmit)(Sph)_2}]^{2-} + 2\,\mathrm{Sph}^-$$

The precursor compound (Me$_4$N)$_2$[M$_4$(Sph)$_{10}$] (M = Zn or Cd), and 4,5-bis(benzoylthio)-1,3-dithiole-2-thione were synthesized as the literature.[12] Preparation of the complexes was performed using Schlenk technique. After deprotection of the ligand in ethanol under argon, the metal cluster of (Me$_4$N)$_2$[M$_4$(Sph)$_{10}$] was added. The mixture was stirred at room temperature until a red precipitate (Me$_4$N)$_2$[M(dmit)(Sph)$_2$] formed. The reaction was complete and gave a pure product. Single brick crystals suitable for X-ray analysis were grown by slow evaporation of the filtrate.

Since dmit is a strong chelate ligand, It attacks the cluster and breaks the metal−thiophenolate bonds. Unlike chloride ion, which is easily displaced, the thiophenolate group also coordinates strongly to the metal center and resists displacement. Thus, the mixed ligand complexes are the predominant product. To our best knowledge, no thiophenolate complexes with dmit have been reported.[1] Thus, complexes **1** and **2** may be the first examples.

X-ray structure determination reveals that the cadmium(II) center of complex **1** involves a CdS$_4$ tetrahedral coordination environment.[13] The structure is illustrated by ORTEP view in Figure 1. The complex has no symmetry center, either as individual molecules or in crystalline form. This character is an important influence on the optical properties of the complexes.

The bond distances of Cd(II) to the sulfur of the thiophenolate group, Cd(1)−S(6) 2.519(2) Å and Cd(1)−S(7) 2.507(1) Å, are shorter than that of Cd(II) to the sulfur of dmit, Cd(1)−S(1) 2.566(2) and Cd(1)−S(2) 2.530(2) Å. That is the reason the thiophenolate group is not replaced during the synthesis, and the mixed

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[10] Physical spectroscopic data for **1** are as follows: Yield 62%, ^{1}H NMR (acetone-d_6, 400 MHz): 3.33 (s, 24H, cation), 6.66 (tri, 2H, ph), 6.82 (tri, 4H, ph), 7.51 (d, 4H, ph). Anal. data for C$_{23}$H$_{34}$N$_2$S$_7$Cd: C, 40.90; H, 5.07; N, 4.15. Found: C, 40.49; H, 4.97; N, 4.06%.

[11] Physical spectroscopic data for **2** are as follows: Yield 57%, ^{1}H NMR (acetone-d_6, 400 MHz): 3.35 (s, 24H, cation), 6.68 (tri, 2H, ph), 6.84 (tri, 4H, ph), 7.51 (d, 4H, ph). Anal. data for C$_{23}$H$_{34}$N$_2$S$_7$Zn: C, 43.96; H, 5.45; N, 4.46. Found: C, 43.51; H, 5.23; N, 4.19%.

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[13] Crystallographic data for **1**: C$_{23}$H$_{34}$N$_2$S$_7$Cd, $M = 675.37$, monoclinic, $P2_1$, $a = 9.534(3)$ Å, $b = 10.626(2)$ Å, $c = 15.079(3)$ Å, $\beta = 91.75(2)°$, $V = 1526.9(5)$ Å^3, $Z = 2$, D (calcd) = 1.469 g cm^{-3}, $R = 0.038$, $R_w = 0.088$, based on 3705 observed reflections $I > 2.00\,\sigma(I)$ and 299 variable parameters.

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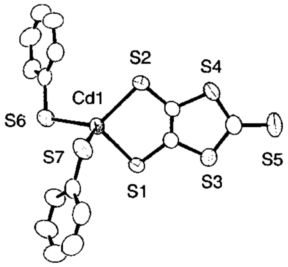

Figure 1. ORTEP view of the complex $(Me_4N)_2[Cd(dmit)(Sph)_2]$ with the atom labeling scheme. Ellipsoids represent 50% probability. Selected bond lengths (Å) and angles (deg): Cd(1)−S(1) 2.566(2), Cd(1)−S(2) 2.530(2), Cd(1)−S(6) 2.519(2), Cd(1)−S(7) 2.507(1), S(1)−Cd(1)−S(2) 88.72(5), S(1)−Cd(1)−S(6) 110.69(6), S(1)−Cd(1)−S(7) 108.26(5), S(2)−Cd(1)−S(6) 118.59(6), S(2)−Cd(1)−S(7) 117.10(6), S(6)−Cd(1)−S(7) 110.77(6).

ligand complexes formed dominantly. The longer Cd−S distances of the chelate ligand dmit can be explained by its rigid structure, because the S(1)−Cd(1)−S(2) angle of 88.72(5)° deviates significantly from the 109° of a tetrahedron. While the monodentate ligand thiophenolate coordinates to the metal without any bond strain, the S(6)−Cd(1)−S(7) angle is just 110.77(6)°.

The C═C and C═S IR stretching bands of the dmit ligand show no significant changes, compared with that of the symmetrical dmit complexes; the S−C−S stretching band at around 890 cm^{-1} for bis(dmit) complexes is shifted to 945 cm^{-1} for complexes **1** and **2**. The electronic spectra of the complex **1** in acetone showed two bands in the 300−700 nm region. The first sharp band at 327 nm is assigned to $\pi-\pi^*$ transition and the band which appears at 512 nm is assigned to $n-\pi^*$ transition of the dmit ligand, compatibly with the spectra of $Na_2(dmit)$ (316, 514 nm in MeOH) and $(Bu_4N)_2[Zn(dmit)_2]$ (300, 530 nm in MeCN).[14]

The third-order optical nonlinearity of the complexes was measured by a phase conjugate forward three-dimensional degenerate four-wave mixing (3D DFWM) technique,[15] using the pulsed laser beam (wavelength 532 nm) from a frequency-doubled picosecond pulse mode-locked Nd:YAG laser. The phase conjugate reflection was detected by PIN photodiode. According to the following formulas, the third-order nonlinear optical susceptibility $\chi^{(3)}$ were obtained by comparing the measured signals for the acetone solution of the complexes with that for carbon disulfide as a reference, under the same experimental conditions. The results are given in Table 1. (No third-order NLO response was found for the pure acetone solvent in the experiment conditions.)

Table 1. Third-Order Nonlinear Optical Properties

complex	C ($\times 10^{-3}$ M)	α/cm^{-1}	measurement width	$\chi^{(3)}$ ($\times 10^{-11}$) esu	$\langle\gamma\rangle$ ($\times 10^{-30}$) esu
1	2.57	28.5	8.82 (20mV)	1.09	2.63
2	2.57	35.5	6.28 (5mV)	1.16	2.80

$$\chi^{(3)} = (I_4/I_{4r})^{1/2}(L_r/L)(n/n_r)^2[\alpha L \exp(\alpha L/2)/(1 - \exp(-\alpha L))]\chi_r^{(3)} \quad (1)$$

$$\langle\gamma\rangle = \chi^{(3)}/L^4N \quad (L^4 = [(n_0^{\ 2} + 2)/3]^4) \quad (2)$$

where the tensor element $\chi_r^{(3)} = 6.8 \times 10^{-13}$ esu for CS_2[16] and the other letters are defined in ref 17.

While some of bis-dithiolene metal complexes have been examined for their third order NLO properties, good results have only been reported for square d^8 metal complexes.[3] Few NLO properties of unsymmetric tetrahedral dithiolene complexes have been reported. The $\chi^{(3)}$ values observed for the complexes **1** and **2** are dependent on the absorption coefficient. The pulsed laser beam at 532 nm is close to the $n-\pi^*$ transition at 512 nm of the complexes; therefore, it can be considered that resonance effects occur and enhance the optical nonlinearity.[18] It is clear that the $\chi^{(3)}$ of the pure solute may be much larger than that of the 10^{-3} M solution, but because of the intense absorption of these complexes, only thin solid films can be used in practical applications.

In summary, we report here a useful new method for the synthesis of unsymmetrical dithiolene metal complexes. By this cluster-cracking method, two complexes $(Me_4N)_2[Cd(dmit)(Sph)_2]$ (**1**) and $(Me_4N)_2[Zn(dmit)(Sph)_2]$ (**2**) were synthesized. Both of the complexes **1** and **2** show modest third-order NLO responses.

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Supporting Information Available: Experiment detail for preparation, characterization of complexes **1** and **2**, and nonlinear optical measurements (PDF). X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) α is the absorption coefficient; L is the thickness of the sample; I is intensity and n is the refractive index; N is molecular density. The subscript r refers to carbon disulfide.

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