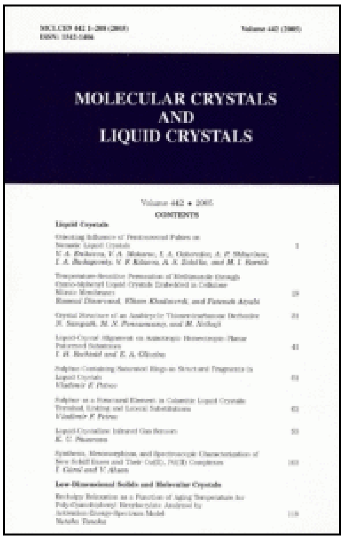

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Crystal Structure and Third-Order Nonlinear Optical Property of a Cadmium Complex Constructed by 1,3-Dithiole-2-Thione-4,5-Dithiolato Ligand

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Crystal Structure and Third-Order Nonlinear Optical Property of a Cadmium Complex Constructed by 1,3-Dithiole-2-Thione-4, 5-Dithiolato Ligand

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A cadmium complex constructed by the ligand 1,3-dithiole-2-thione-4,5-dithiolato (DMIT) has been synthesized and its structure has been determined by means of X-ray single crystal diffraction. Crystal data for this complex are as follows: monoclinic, space group Cc, $a = 24.590(2)$, $b = 8.7882(7)$, $c = 13.8032(11)$ *Å,* $\beta = 116.3350(10)^\circ$, $V = 2{,}673.3(4)$ *Å*^{3}, $Z = 4$, $F(000) = 1{,}188$. *The central cadmium ion coordinates with two DMIT which constructed a distorted tetrahedron. Its third-order nonlinear optical property has been studied using Z-scan technique with 20 ps pulses at wavelength 1,064 nm. Its molecular second hyperpolarizability* γ *was determined to be* 3.96×10^{-55} $C{\bullet}m^4/V^3$.

Keywords Cadmium(III) complex; crystal structure; third-order nonlinear optical property; Z-scan

Introduction

Third-order nonlinear optical materials have attracted much attention because of their potential utilities in ultrafast optical switching and modulations, optical storing, etc., and various types of metal-organic compounds have been synthesized and studied to obtain materials with large third-order susceptibilities $\chi^{(3)}$ [1,2]. The third-order nonlinear optical properties of the complexes constructed by the DMIT ligand have been paid much attention during recent past years [3], because the results shown this kind of complex possesses fine third-order nonlinear optical property. In this article, the single-crystal structure and third-order nonlinear optical properties of a cadmium complex are reported.

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Experimental Methods

Synthesis and Recrystallization of $[(CH_3)_4N][Cd(DMIT)_2] \cdot H_2O$

The synthesis method was the same as in Steimecke *et al.* [4], which was first described in 1977. All chemicals were purchased from commercial sources and used without further purification. Single crystals suitable for X-ray structure determination were obtained by recrystallization in acetonitrile solution.

X-Ray Crystallographic, Infrared Spectrum, and Linear Absorption Spectra Study

Structure determination was performed on a Bruker Smart Apex II CCD X-ray diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) for data collection by using an Φ and ω scan mode at 293(2) K. A total of 5,642 reflections (3,241 independent ones with $R_{\text{int}} = 0.0401$, $R_{\text{sigma}} = 0.0936$) were collected in the range of $3.7 < 2\theta < 50.08°$, of which 2,461 observed reflections with $I > 2\sigma(I)$ were used in the structural analysis. Absorption corrections were applied using the SADABS program [5]. The structure was solved by direct methods and refined by full-matrix least-squares calculations for 208 parameters. All the calculations were carried out with SHELXL-97 program [6] with anisotropic thermal parameters for the nonhydrogen atoms. All hydrogen atoms were placed in the calculated positions and refined isotropically using a riding model. The final $R = 0.1000$, $wR = 0.2621$ ($\omega = 1/[\sigma^2(F_0^2) + (0.2250P)^2 + 0.9990P]$ where $P = (F_0^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{\max} = 0.002$, $S = 0.997$. CCDC-717474 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html.

The IR spectrum was recorded on a Nicolet 6700 spectrophotometer in the region of 400–4,000 cm^{-1} with a KBr pellet technique. Its linear absorption spectra in acetonitrile solution at a concentration of 1.22×10^{-5} mol/L were recorded at 20°C with a Hitachi U-4100 spectrophotometer.

Third-Order Nonlinear Optical Property Measurements

The third-order nonlinear optical property measurements were performed using single beam closed-aperture Z-scan technique [7] in an acetonitrile solution of 3.51×10^{-3} mol/L. The light source was a mode-locked Nd:YAG laser (Continuum Leopard D-10, 20 ps, 10 Hz, 1,064 nm), and the focal length of the positive lens was f = 30 cm. The transmitted energy was measured using a Molectron J3–10 detector in combination with EPM2000 energy meter in the far field.

Results and Discussion

Crystal Structure of $[(CH_3)_4N][Cd(DMIT)_2] \cdot H_2O$

The motif structure of the titled complex's single crystals is shown in Fig. 1. The cadmium ion was coordinated with four sulfur atoms of two DMIT ligands, which constructed a distorted tetrahedron. The Cd(1)-S(10), Cd(1)-S(9), Cd(1)-S(4), and Cd(1)-S(5) bond lengths were 2.485(7), 2.539(8), 2.505(9), and 2.545(7) Å, and the S(10)-Cd(1)-S(4), S(10)-Cd(1)-S(9), S(4)-Cd(1)-S(9), S(10)-Cd(1)-S(5), S(4)-Cd(1)-S(5), and S(9)-Cd(1)-S(5) bond angles were 130.4(3)°, 89.4(2)°, 119.1(3)°, 118.2(3)°,

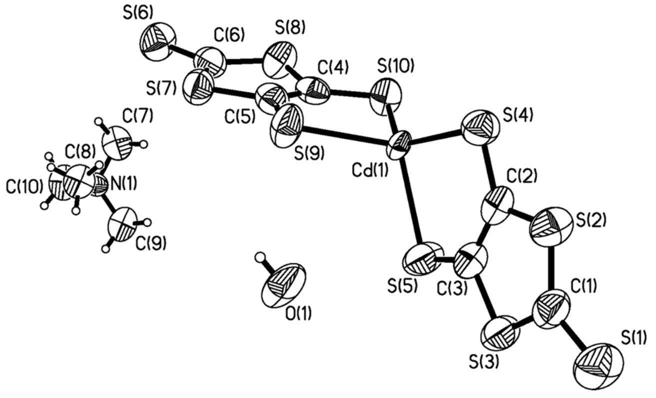

Figure 1. Motif structure of $[(CH_3)_4N][Cd(DMIT)_2]\cdot H_2O$ single crystals, with thermal ellipsoids set at 30% probability.

89.6(3)°, and 111.8(4)°, which are in the common range [8]. The bond lengths and angles of the DMIT were as expected [9]; the S(1) = C(1) was 1.66(3) Å, C(1)-S(2) was 1.63(4) Å, S(2)-C(2) was 1.76(3) Å, S(3)-C(3) was 1.72(3) Å, S(3)-C(1) was 1.84(4) Å, S(4)-C(2) was 1.70(3) Å, S(5)-C(3) was 1.75(3) Å, and C(2) = C(3) was 1.40(4) Å. Fig. 2 shows the crystal packing diagram that viewed from the *a* axis, for clarity the H_2O was deleted.

IR Spectrum and Linear Absorption Spectra

Figure 3 shows the IR spectrum. The major IR peaks of the complex were consistent with the structural results. The intense bands at 1,477.3 and 1,404.9 cm^{-1} were assigned to the C=C stretching vibrations. The intense band at 1,059.3 cm^{-1} was assigned to C=S terminal stretching vibrations. These bands are generally used to confirm the presence of DMIT ligands in complexes [10]. Other bands and assignments are as follows: 984.5, 945.9, 904.7, and 871.0 cm^{-1} due to ν(C-S) vibrations; and the low-intensity band at 528.2 cm^{-1} is a breathing mode of the DMIT heterocycle; and 459.6 cm^{-1} due to ν(Cd-S) vibration. Figure 4 shows the linear absorption spectra. From the figure one can see that there are two main absorptive bands located around 375 and 480 nm; the former can be attributed to $\pi \rightarrow \pi^*$ electron transitions and the latter one may be attributed to metal-ligand charge transfer (MLCT) transitions.

Third-Order Nonlinear Optical Property

Figure 5 shows the normalized closed-aperture Z-scan measurement results; the theoretical results were drawn as the pentacle line. For the closed-aperture Z-scan measurement results, the normalized transmittance T relates position z through equation (1) [7,11,12]:

$$T(x,\Delta\phi_0) = 1 + \frac{4x}{(x^2+9)(x^2+1)}\Delta\phi - \frac{(3-x^2)}{(x^2+9)(x^2+1)}\Delta\psi \qquad (1)$$

where $x = z/z_0$, $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range of the beam. $\Delta\phi = kn_2^{\mathrm{I}} I_0 L_{eff}$ is the phase shift derived from nonlinear refraction, and $\Delta\psi = \beta I_0 L_{eff}/2\sqrt{2}$ is the phase

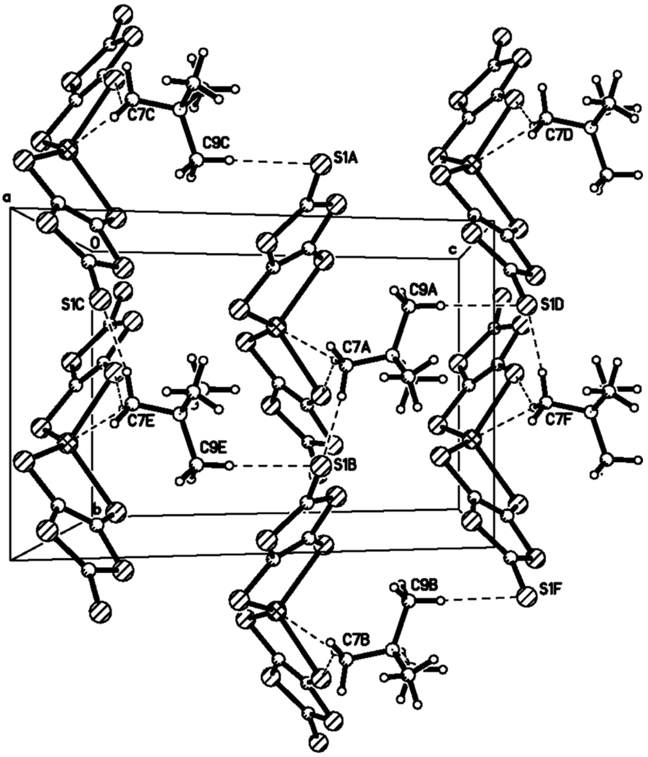

Figure 2. Crystal packing, viewed from the *a* axis. For clarity the H_2O molecular was deleted.

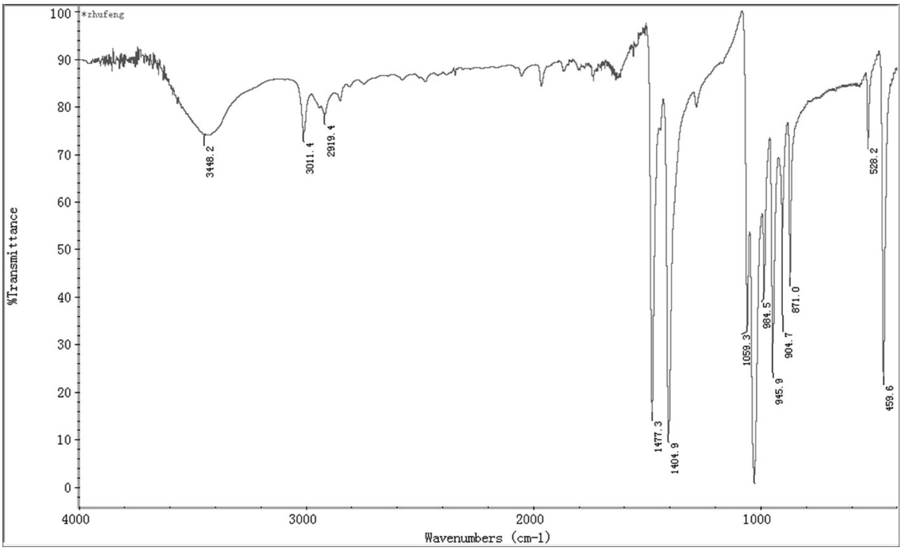

Figure 3. IR spectrum of $[(CH_3)_4N][Cd(DMIT)_2] \cdot H_2O$.

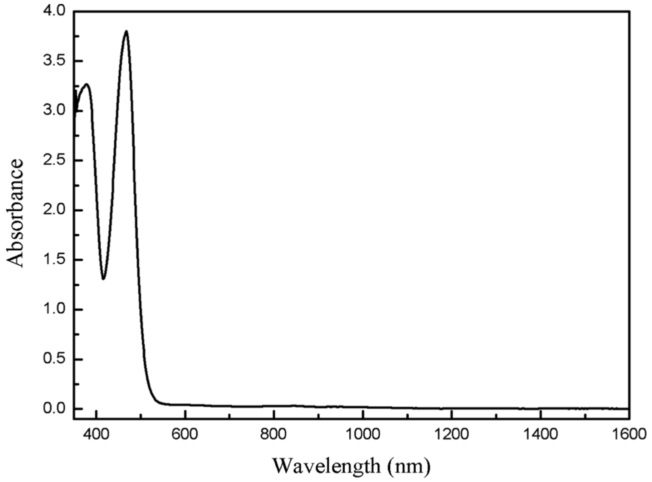

Figure 4. Linear absorption spectra of $[(CH_3)_4N][Cd(DMIT)_2]\cdot H_2O$ in acetonitrile solution.

shift derived from nonlinear absorption. $k = 2\pi/\lambda$ is the wave vector. I_0 is the peak intensity, which relates the pulse energy ξ through the Eq. [13]. $I_0 = 4\sqrt{\ln 2}\xi/\pi^{3/2}\omega_0^2\tau$. $L_{eff} = (1 - e^{-\alpha_0 l.})/\alpha_0$ is effective sample length. The imaginary part of the $\chi^{(3)}$ is related to β through $\chi_I^{(3)} = \frac{\varepsilon_0 n_0^2 c\lambda}{3\pi}\beta$ (SI) and the real part of the $\chi^{(3)}$ is related to n_2^I through $\chi_R^{(3)} = 2n_2^I n_0^2 \varepsilon_0 c$ (SI), where $\varepsilon_0 = 8.85 \times 10^{-12}\ c^2/N\cdot m^2$ is the electric permittivity of free space, n_0 is the linear refractive index, c is the light speed of free space and λ is the wavelength. So the $\chi^{(3)}$ can be determined through the equation $\chi^{(3)} = \sqrt{(\chi_R^{(3)})^2 + (\chi_I^{(3)})^2}\ (m^2/V^2)$. The molecular second hyperpolarizability γ is related to $\chi^{(3)}$ through the equation $\gamma(m^4C/V^3) = \frac{\varepsilon_0}{f^4 N}\chi^{(3)}(m^2/V^2)$ and $f = n_0^2 + 2/3$ is the local field factor. All the results are shown in Table 1.

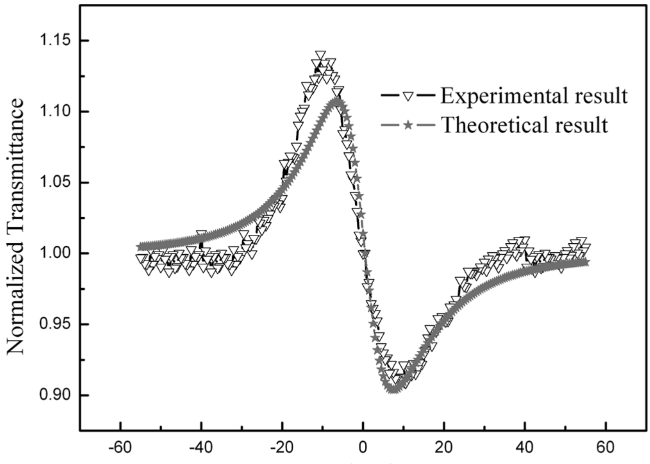

Figure 5. Normalized closed-aperture Z-scan of $[(CH_3)_4N][Cd(DMIT)_2]\cdot H_2O$ solution in acetonitrile (3.51×10^{-3} mol/L) that were filled in a 1-mm path-length quartz cuvette using 20-ps pulses at $\lambda = 1{,}064$ nm. The pentacle line is the theoretical results.

Table 1. Third-order nonlinear optical properties of $[(CH_3)_4N][Cd(DMIT)_2] \cdot H_2O$

n_2^I ($\times 10^{-18}$ m^2/W)	$\chi_R^{(3)}$ ($\times 10^{-20}$ m^2/V^2)	β ($\times 10^{-10}$ m/W)	$\chi_I^{(3)}$ ($\times 10^{-19}$ m^2/V^2)	$\chi^{(3)}$ ($\times 10^{-19}$ m^2/V^2)	γ ($\times 10^{-55}$ $C \cdot m^4/V^3$)
−2.86	−2.72	4.48	2.41	2.42	3.96

Conclusions

In conclusion, a cadmium complex has been synthesized and its structure has been determined by means of X-ray single-crystal diffraction. Its third-order nonlinear optical properties were studied using a closed-aperture Z-scan technique. As the results show, it possesses better third-order nonlinear optical properties and has promising applications in ultrafast optical switching and modulations, optical limiting, fluorescence excitation microscopy and imaging, three-dimensional optical data storage, etc.

Acknowledgment

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