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### Synthesis, Crystal Structure, Spectroscopy and Calculated First-Order Molecular Hyperpolarizability of a New Square-pyramidal Complex Zn(DMABT)(acac) 2

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# SYNTHESIS, CRYSTAL STRUCTURE, SPECTROSCOPY AND CALCULATED FIRST- ORDER MOLECULAR HYPERPOLARIZABILITY OF A NEW SQUARE-PYRAMIDAL COMPLEX **Zn(DMABT)(acac)<sub>2</sub>**

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A new square-pyramidal complex, Zn(DMABT)(acac)<sub>2</sub> (DMABT = *p*-dimethylaminobenzaldehyde thiosemicarbazone; acac = acetylacetonate), has been synthesized and characterized by IR, <sup>1</sup>H NMR, elemental analysis and X-ray crystal structure analysis. Crystal data: crystal system Monoclinic, space group *P*2<sub>1</sub>/*n*, with *M<sub>r</sub>* = 485.89 (C<sub>20</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>SZn), *a* = 8.208(3) Å, *b* = 10.982(5) Å, *c* = 26.647(9) Å,  $\alpha = 90^\circ$ ,  $\beta = 93.67(3)^\circ$ ,  $\gamma = 90^\circ$ , *V* = 2396.8(15) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.347 g/cm<sup>3</sup>, *F*(000) = 1016,  $\mu = 1.143 \text{ mm}^{-1}$ , *R*<sub>1</sub> = 0.0444, *wR*<sub>2</sub> = 0.1182. Reflections collected are 4733, while unique reflections are 4636 with *I* ≥ 2σ(*I*). The complex structure contains a square-pyramid formed by four oxygen atoms and one sulfur atom around a zinc atom. The molecular shape is like a screw, in which two acetylacetonate groups form the head and the DMABT group forms the tail. The first-order molecular hyperpolarizabilities ( $\beta$ ) of the complex and DMABT were calculated utilizing PM3 method through MOPAC software package in Chem 3D, the result of which shows that the  $\beta_0$  value of the complex ( $30.6 \times 10^{-30}$  esu) is higher than that of DMABT ( $21.5 \times 10^{-30}$  esu). Electronic absorption spectroscopy was compared with ZINDO/S calculated result.

*Keywords:* Zn(II); Synthesis; Crystal structure; Hyperpolarizability; Calculation

## INTRODUCTION

Molecular materials have played an important role in many fields of materials science such as magnets, conductors and nonlinear optical (NLO) materials, due to the opportunity to modify and optimize the solid state properties through modification at the molecular level [1,2]. For second-order NLO materials, much attention has focused on the inorganic complex because of its capacity to enhance molecular first-order hyperpolarizability ( $\beta$ ) through intramolecular metal-to-ligand or ligand-to-metal charge transfer processes, and to increase the ratio of asymmetric structures because

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of the diverse coordination styles between metal and ligand [3–5]. We, and others, have investigated a series of screw-shaped square-pyramidal complexes  $\text{ZnL}(\text{acac})_2$  ( $\text{acac} = \text{acetylacetonato}$ ), and found two,  $\text{Zn}(\text{PTU})(\text{acac})_2$  ( $\text{PTU} = \text{phenylthiourea}$ ) ( $\text{PZDA}$ ) and  $\text{Zn}(\text{DMAP})(\text{acac})_2$  ( $\text{DMAP} = p\text{-dimethylaminopyridine}$ ) ( $\text{ZND A}$ ), which exhibit second harmonic generation (SHG) ten times and twice as large as that of KDP (potassium dihydrogen phosphate), respectively [6–8]. In this article, we present the synthesis, crystal structure and calculated  $\beta$  value of another screw-shape square-pyramidal complex  $\text{Zn}(\text{DMABT})(\text{acac})_2$  ( $\text{DMAPT} = p\text{-dimethylaminobenzaldehyde thiosemicarbazone}$ ).

## EXPERIMENTAL

All chemicals used were analytical grade and used as received without further purification. Acetonediacylacetonatozinc(II),  $(\text{CH}_3)_2\text{CO} \cdot \text{Zn}(\text{acac})_2$ , was synthesized as previously [9].

### Physical Measurements

IR spectra were recorded on a NICOLET 170SX FT-IR spectrometer.  $^1\text{H}$  NMR spectroscopy was performed on a MERCURY-VX300 with  $\text{DMSO}-d_6$  as the solvent. Elemental analysis was obtained on a Calo-Erba elemental analyser (Model 106). The electronic spectra of the complexes in the UV-visible region were recorded on a SCHIMADZU UV-160A spectrophotometer.

### *p*-Dimethylaminobenzaldehyde Thiosemicarbazone (DMABT)

1.82 g (0.02 mol) thiosemicarbazide was added to a refluxing ethanol solution of 2.98 g (0.02 mol) *p*-dimethylaminobenzaldehyde. The solution was further refluxed for about 5 h, and on cooling light yellow crystalline precipitate was formed, which was then filtered off under low pressure and washed several times with ethanol. The product was recrystallized from methanol and dried under vacuum for about 4 h; yield 3.9 g (87.7 %). IR data ( $\text{KBr}, \text{cm}^{-1}$ ): 3373.3, 3330.8, 3249.8 ( $\text{NH}_2$ , s), 3151.5 ( $\text{NH}$ , s); 2900.7, 2858.3, 2815.9 ( $\text{CH}_3$ , m); 1595.0, 1504.4 ( $\text{C}=\text{N}$ , Ar-H, s); 1182.3 ( $\text{C}=\text{S}$ , s). Anal. calcd. for DMABT ( $\text{C}_{10}\text{H}_{14}\text{N}_4\text{OS}$ ): C, 54.0; H, 6.3; N, 25.2. Found: C, 54.3; H, 6.5; N, 25.7.

### Preparation of $\text{Zn}(\text{DMABT})(\text{acac})_2$

0.22 g (1 mmol) DMABT was added to the acetone-acetyl acetone (1:1) solution of 0.33 g (1 mmol)  $(\text{CH}_3)_2\text{CO} \cdot \text{Zn}(\text{acac})_2$  at  $50^\circ\text{C}$ . The mixture was reacted for about 1 h to get yellow precipitate, which was then filtered off and dried under vacuum; yield 0.30 g (61.2 %). Single crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of an acetone-acetyl acetone (1:1) solution of the product in air. IR data ( $\text{KBr}, \text{cm}^{-1}$ ): 3431.1, 3147.6 ( $\text{NH}_2$ , s); 3263.3 ( $\text{NH}$ , m); 2989.5, 2960.5, 2918.1, 2850.6 ( $\text{C}-\text{H}$ , m); 1610.5 ( $\text{C}=\text{N}$ , s); 1591.2, 1562.2, 1519.8 (Ar-H, s); 1180.4 ( $\text{C}-\text{O}$ , s); 1016.4 ( $\text{C}=\text{S}$ , m); 821.6 (Ar-H, m).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  ppm, 1.8 (s, 12H), 2.9 (s, 6H), 5.2 (s, 2H), 6.6–6.7 (d, 2H), 7.5–7.6 (d, 2H), 7.8 (s, 2H), 7.9

(s, 1H), 11.1 (s, 1H). Anal. calcd. for Zn(II)(DMABT)(acac)<sub>2</sub> (C<sub>20</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>SZn)%: N, 11.5; C, 49.2; H, 6.2. Found: N, 11.9; C, 50.4; H, 6.5.

### Crystallographic Structure Determination

A single crystal with dimensions 1.10 mm × 0.80 mm × 0.40 mm was mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The data were collected at 293 K using the  $\omega/2\theta$  scan mode and corrected for Lorentz and polarization effects as well as absorption during data reduction using Enraf-Nonius Molen/VAX Software. 4733 reflections were collected in the range  $4.82^\circ < 2\theta < 51.94^\circ$ , while unique reflections were 4636 with  $I \geq 2\sigma(I)$ . The complex is monoclinic, and space group is  $P2_1/n$ , with  $M_r = 485.89$ ,  $a = 8.208(3) \text{ \AA}$ ,  $b = 10.982(5) \text{ \AA}$ ,  $c = 26.647(9) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 93.67(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2396.8(15) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.347 \text{ g/cm}^3$ ,  $F(000) = 1016$ ,  $\mu = 1.143 \text{ mm}^{-1}$ .

The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. All computations were carried out using SHELXTL [10]. The final  $R$  and  $R_w$  ( $w = 1/\sigma^2$ ) were 0.0444 and 0.1182, respectively. The maximum shift/esd and largest peak in the final difference Fourier map were 0.002 and  $0.507 \text{ e \AA}^{-3}$ .

### Calculation of the Second-order NLO Response

All calculations were performed on a PC Pentium III 750 MHz. The all-valence ZINDO/S (intermediate neglect of differential overlap) method in Hyperchem 5.11 software package (Hypercube, Florida) [11] was employed to calculate electronic spectra. Details of the ZINDO method for calculating electronic spectra and second-order molecular NLO properties can be found elsewhere [12]. The molecular hyperpolarizability was calculated using PM3 parameterization in the MOPAC software package (7.0) [13]. The closed-shell restricted Hartree-Fock (RHF) formalism was employed. The monoexcited configuration interaction (MECI) approximation was used to describe the excited states. The ten highest occupied molecular orbitals and the ten lowest unoccupied molecular orbitals were involved in CI mixing. The molecular structure was optimized utilizing AMI parameterization.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

The ligand DMABT was prepared by the condensation reaction between *p*-dimethylaminobenzaldehyde and thiosemicarbazide in 1:1 mole ratio. The synthesis can be monitored by IR spectra to verify the disappearance of the carbonyl signals. The formation of the complex was to substitute the acetone group in the acetonediacetyl-acetonatozinc(II) complex with DMABT by direct reaction in acetone-acetyl acetone (1 : 1) mixed solvent. The red shift of the C=S absorption peak (from  $1182.3 \text{ cm}^{-1}$  to  $1016.4 \text{ cm}^{-1}$ ) indicates the formation of a coordination bond between the S atom and the Zn atom. Formation of the complex can also be supported by the appearance of peaks at 1.8 ppm(s, 12H) and 5.2 ppm(s, 2H) in  $^1\text{H}$  NMR spectra, which are the characteristic peaks of acac group.

### Crystal Structure Description of the Complex

The ORTEP drawing of the complex with numbered atoms is shown in Fig. 1. Figure 2 shows the crystal packing along the *a* direction. Atomic coordinates for non-hydrogen atoms are listed in Table I. Some selected bond lengths and angles are given in Table II, and hydrogen bonds formed are shown in Table III. Zinc is coordinated to four oxygen atoms of the acac groups and one sulfur atom of DMABT ligand to form a distorted

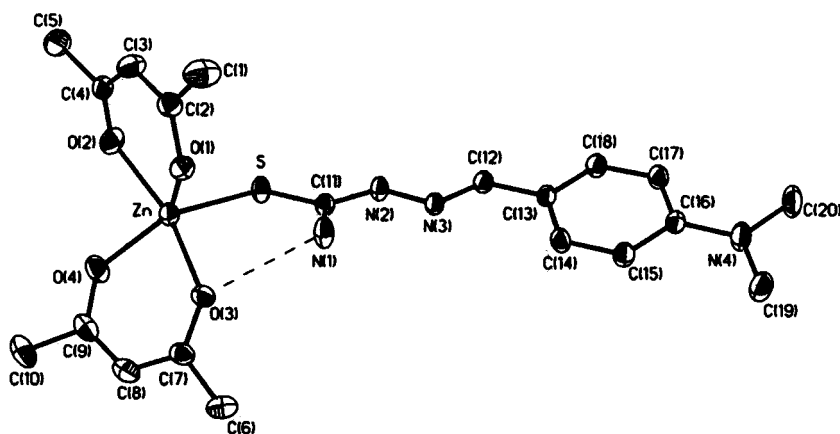


FIGURE 1 ORTEP view of the molecular structure of the complex.

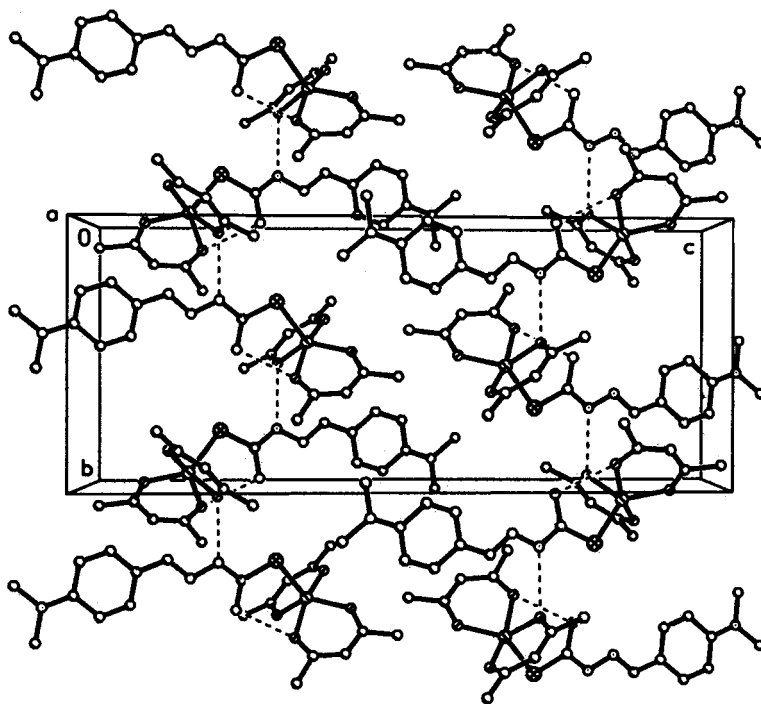


FIGURE 2 Crystal packing along *a* direction.

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

Atom	x	y	z	$U_{\text{eq}}$
Zn	1778(1)	14557(1)	3431(1)	47(1)
S	2984(1)	12984(1)	2962(1)	54(1)
O(1)	227(2)	15397(2)	2923(1)	51(1)
O(2)	-142(3)	13627(2)	3687(1)	67(1)
O(3)	3328(3)	15958(2)	3274(1)	58(1)
O(4)	2306(3)	14930(2)	4158(1)	73(1)
N(1)	3524(4)	14857(2)	2338(1)	65(1)
N(2)	4142(3)	12958(2)	2075(1)	49(1)
N(3)	4721(3)	13495(2)	1651(1)	48(1)
N(4)	7851(4)	14266(3)	-473(1)	69(1)
C(1)	-1948(5)	15614(4)	2316(2)	88(1)
C(2)	-1218(4)	15041(3)	2789(1)	55(1)
C(3)	-2097(4)	14212(3)	3050(1)	68(1)
C(4)	-1562(4)	13601(3)	3490(1)	56(1)
C(5)	-2771(5)	12852(4)	3763(2)	90(1)
C(6)	5331(5)	17495(4)	3335(2)	88(1)
C(7)	4249(4)	16578(3)	3575(1)	57(1)
C(8)	4259(4)	16497(3)	4090(1)	68(1)
C(9)	3251(5)	15737(3)	4354(1)	67(1)
C(10)	3210(6)	15890(5)	4915(1)	95(1)
C(11)	3580(3)	13675(2)	2425(1)	45(1)
C(12)	5106(3)	12752(3)	1310(1)	48(1)
C(13)	5799(3)	13159(3)	853(1)	47(1)
C(14)	6257(4)	14366(3)	779(1)	54(1)
C(15)	6933(4)	14731(3)	349(1)	58(1)
C(16)	7157(3)	13904(3)	-42(1)	49(1)
C(17)	6680(4)	12690(3)	29(1)	55(1)
C(18)	6028(4)	12342(3)	468(1)	54(1)
C(19)	8333(5)	15527(3)	-543(1)	73(1)
C(20)	7999(6)	13442(4)	-883(1)	95(1)

square-pyramid. The Zn–O distances are 2.022(2) Å, 2.032(2) Å, 2.057(2) Å and 1.998(2) Å, respectively, while the S–Zn bond length is 2.3845(10) Å. The C(11)–S bond length is 1.717(3) Å, which is between 1.82 Å for a C–S single bond and 1.56 Å for a C=S double bond [14]. The whole molecule can be seen as a screw, in which two acetylacetonato groups form the head and DMABT forms the long tail.

From Figure 2, it is clear that there are four molecules within one crystal unit cell. The whole crystal structure is stabilized by intermolecular and intramolecular hydrogen bonds (Table III). The hydrogen bond formed between N(1)–H(1B) and O(3) belongs to intramolecular hydrogen bond (bond length 2.02 Å), while the hydrogen bond N(2)–H(2A) . . . O(1)#1 ( $-x + 0.5, y - 0.5, -z + 0.5$ ) (2.03 Å) belongs to intermolecular hydrogen bond. The intramolecular hydrogen bond makes the DMABT ligand bend to one side and close to one acac group. This is different from the previously reported screw-shaped SHG-active  $\text{ZnL}(\text{acac})_2$  complexes, in which L ligands always choose a perpendicular configuration [6,8]. In those cases, the molecules strictly form a head-to-tail backbone along dipole moment direction, and there are little lateral interactions between the backbones. This crystal lattice benefits the formation of an asymmetric structure which is essential to second-order NLO materials [8,15]. The somewhat flexible long chain of the DMABT ligand probably causes the complex structure to deviate from the polar assembly.

TABLE II Selected bond lengths (Å) and angles (°)

Bond lengths (Å)		Bond angles (°)	
Zn–O(4)	1.998(2)	O(4)–Zn–O(1)	130.06(10)
Zn–O(1)	2.022(2)	O(4)–Zn–O(2)	84.42(11)
Zn–O(2)	2.032(2)	O(1)–Zn–O(2)	89.16(9)
Zn–O(3)	2.057(2)	O(4)–Zn–O(3)	86.86(10)
Zn–S	2.3845(10)	O(1)–Zn–O(3)	83.86(9)
S–C(11)	1.717(3)	O(2)–Zn–O(3)	161.32(10)
O(1)–C(2)	1.278(4)	O(4)–Zn–S	125.83(9)
O(2)–C(4)	1.248(4)	O(1)–Zn–S	104.09(7)
O(3)–C(7)	1.266(4)	O(2)–Zn–S	99.73(8)
O(4)–C(9)	1.268(4)	O(3)–Zn–S	98.77(7)
N(1)–C(11)	1.318(4)	C(11)–S–Zn	105.48(10)
N(2)–C(11)	1.326(3)	C(2)–O(1)–Zn	125.56(19)
N(2)–N(3)	1.385(3)	C(4)–O(2)–Zn	126.4(2)
N(3)–C(12)	1.277(4)	C(7)–O(3)–Zn	128.7(2)
N(4)–C(16)	1.373(4)	C(9)–O(4)–Zn	129.2(2)
N(4)–C(20)	1.430(5)	C(11)–N(2)–N(3)	118.2(2)
N(4)–C(19)	1.455(4)	C(12)–N(3)–N(2)	115.0(2)
C(1)–C(2)	1.498(5)	N(1)–C(11)–S	124.9(2)
C(2)–C(3)	1.379(5)	N(2)–C(11)–S	117.0(2)

TABLE III Hydrogen bonds (Å and °)

<i>D–H...A</i>	<i>d(D–H)</i>	<i>d(H...A)</i>	<i>d(D...A)</i>	<i>&lt;(DHA)</i>
N(1)–H(1B)...O(3)	0.86	2.02	2.785(3)	148.1
N(2)–H(2A)...O(1)#1	0.86	2.03	2.860(3)	162.6

Symmetry transformations used to generate equivalent atoms: #1 –  $x + 1/2, y - 1/2, -z + 1/2$ .

TABLE IV Electronic absorption spectroscopy and calculation of  $\beta$  value

	$\lambda_{max}$ (nm)		$\beta_0$ ( $\times 10^{-30}$ esu)
	Experiment	Calculation	
Complex	364	311      271	30.6
DMABT	365	\      \	21.5

### Electronic Absorption Spectroscopy and Calculation of $\beta$ Value

The results of ZINDO/S calculation and experimental absorption maximum in chloroform solution are listed in Table IV. The experimental optical spectra data and calculated ZINDO/S derived electronic spectrum of the complex are compared in Fig. 3. Calculation shows that there are mainly two absorption maxima at 311 nm ( $f = 1.107$ ) and 271 nm ( $f = 0.620$ ). The agreement between calculation and experiment is rather good, although there exists 10–40 nm error in  $\lambda_{max}$  between calculated and experimental data, which is within the error range of ZINDO/S calculation for other types of complexes [16,17].

PM3 method in MOPAC97 software package has been used to calculate the  $\beta$  values of the complex and DMABT ligand. Table IV lists the calculation results, from which comparing to the DMABT ligand, the  $\beta_0$  of the complex increases (from  $21.5 \times 10^{-30}$  to  $30.6 \times 10^{-30}$  esu), indicating that the intramolecular charge transfer between metal

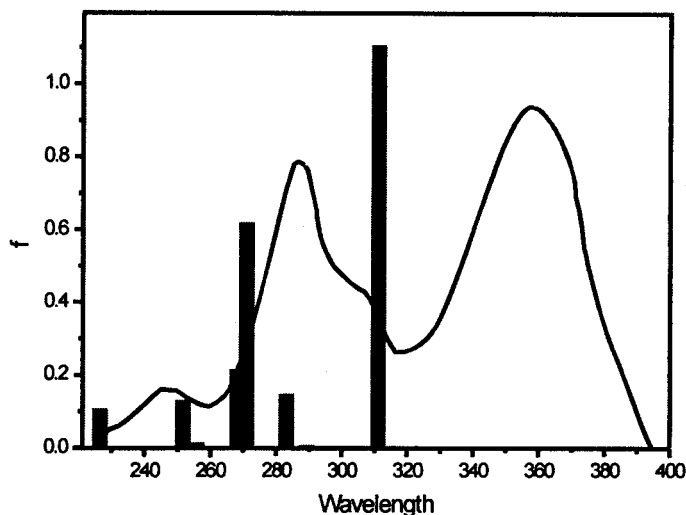


FIGURE 3 The experimental optical spectra data and ZINDO/S derived electronic spectrum of the complex.

and ligand is beneficial to the first-order molecular hyperpolarizability. It is noticeable that while  $\beta_0$  increases upon coordination, the absorption maximum ( $\lambda_{\max}$ ) of the complex and ligand are almost the same (364 nm for the former, 365 nm for the latter), which may provide valuable information for the solution of so-called transparency-nonlinearity trade-off.

### Acknowledgment

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### Supplementary Materials

Tables of hydrogen atom coordinates, thermal parameters, full lists of bond lengths and angles, and other crystal structure data are available from the authors.

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