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A new approach to suppress nonlinearity-transparency trade-off through coordination chemistry: syntheses and spectroscopic study on second-order nonlinear optical properties of a series of square-pyramidal zinc(II) complexes

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Abstract

Five new square-pyramidal coordination compounds L · Zn(acac)₂ (1–5) (acac = acetylacetonate; L is a variety of thiosemicarbazones: *p*-dimethylaminobenzaldehyde thiosemicarbazone (1), *p*-hydroxy-*o*-methoxybenzaldehyde thiosemicarbazone (2), *p*-methoxybenzaldehyde thiosemicarbazone (3), *p*-hydroxybenzaldehyde thiosemicarbazone (4), *o*-hydroxybenzaldehyde thiosemicarbazone (5)) have been synthesized and characterized by ¹H NMR, IR, and elemental analysis. All of these compounds exhibit pretty wide transparent ranges in the visible region. Their electronic absorption spectra have been studied experimentally, and theoretically by ZINDO/S calculation. The latter has also been utilized to estimate the extent of intramolecular charge transfer. The MOPAC software package has been used to evaluate their first-order molecular hyperpolarizabilities (β). All β values of the five coordination compounds are larger than those of the corresponding thiosemicarbazones. And complex 1 shows the largest β_0 (39.1 × 10⁻³⁰ esu) in the series. (C) 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Second-order nonlinear optical (NLO) materials have been attracting considerable attention due to their broad applications in optoelectronics, such as optical frequency conversion [1,2] and optical

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parameter oscillator (OPO) [3]. It has long been recognized that molecular chromophores could exhibit a second-order NLO response several orders of magnitude larger than that of inorganic compounds, such as potassium dihydrogen phosphate (KDP) and lithium niobate (LN) [4,5]. To search for new molecular chromophores people have paid attention to coordination systems in recent years, as they can offer a large variety of molecular structures by changing metals, ligands

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Scheme 1. Synthetic route of the complexes.

or coordination numbers, to enhance thermal stability, and to diverse electronic behaviors by virtue of the coordinated metal center [6-8]. Up to now, many organometallic and coordination compounds exhibiting large first-order molecular hyperpolarizabilities have been synthesized [6]. Most of them have absorption bands in visible region due to the so-called optical nonlinearity-transparency trade-off.

On the basis of more than 10 years' research on organometallic and coordination NLO materials, we have summarized an empirical rule [9] indicating that the molecular configuration is definitely an important factor to affect the linear and nonlinear optical properties of coordination compounds. It seems that involvement of the metal ions with d^{10} electron structure (such as Zn(II), Cd(II) and Hg(II)) can cause excellent transparency in the visible region, as the metal ions do not form an efficient electron conjugation system with the ligands, and thus is hardly involved in the intramolecular charge transfer. In addition, they do not perform d-d excitation themselves [9]. Phenylthiourea zinc diacetylacetonate (PZDA) [10], a square-pyramidal coordination compound, which shows excellent transparency in the visible region and a second harmonic generation (SHG) of ten times as large as that of KDP, is a successful application of the empirical rule.

As a continuation of the research on finding new coordination compounds exhibiting both large second-order NLO effects and good transparency, herein we report on a study of utilizing thiosemicarbazones, which have been proposed as coordination ligands for nonlinear optical materials because of their pale colors, thermally stability and excellent coordination capabilities [11], as ligands, to form a series of novel pyramidal zinc(II) coordination compounds 1-5 (Scheme 1). We hope to provide valuable information to the optimization of the optical nonlinearity–transparency trade-off.

2. Experimental

The general synthetic route contains mainly three steps, including the formation of acetone zinc diacetylacetonate (acetone-ZDA); the formation of thiosemicarbazones; and the preparation of the final coordination compounds (Scheme 1). All of the chemicals used were of analytical reagent (A.R.) grade. Acetone-ZDA was synthesized according to the reference [12].

2.1. Physical measurements

Infrared (IR) spectra were recorded on a NICO-LET 170SX FT-IR spectrometer. Nuclear magnetic resonance (NMR) was performed on a MERCURY-VX300 spectrometer. The elemental analysis was obtained on a Calo–Erba elemental analyzer (Model 106). The electronic spectra of the complexes in the ultraviolet-visible (UV-vis) region were recorded in a SCHIMADZU UV-160A spectrophotometer.

2.2. Preparation of thiosemicarbazones

Thiosemicarbazones were prepared by condensation of the appropriate substituted benzaldehyde with thiosemicarbazide (1:1 molar ratio) in ethanol, and purified by recrystallization from methanol (yields 80–90%).

2.2.1. *p*-Dimethylaminobenzaldehyde thiosemicarbazone

IR data (KBr, cm⁻¹): 3373.3, 3151.5 (s, N–H, NH₂), 3249.8 (s, N–H, NH); 2900.7, 2858.3, 2815.9 (m, C–H, CH₃, CH); 1605.5 (s, C=N); 1595.0, 1504.4 (s, C–C, phenyl); 1182.3 (s, C=S). Elemental Anal. (%) Calc.: C, 54.0; H, 6.3; N, 25.2. Found: C, 54.3; H, 6.5; N, 25.7.

2.2.2. *p*-Hydroxy-o-methoxybenzaldehyde thiosemicarbazone

IR data (KBr, cm⁻¹): 3525.6 (s, OH); 3435.0, 3153.4 (s, N–H, NH₂), 3276.8 (s, N–H, NH); 2968.2, 2933.5, 2839.0 (m, C–H, CH₃, CH); 1591.2, 1544.9, 1514.0 (s, C–C, phenyl); 941.2 (s, C=S). Elemental Anal. (%) Calc.: C, 48.0; H, 4.9; N, 18.7. Found: C, 47.7; H, 5.4; N, 18.6.

2.2.3. p-Methoxybenzaldehyde thiosemicarbazone

IR data (KBr, cm⁻¹): 3402.2, 3153.4 (s, N–H, NH₂); 3288.4 (s, N–H, NH); 2962.5, 2925.8 (m, C–H, CH₃, CH); 1602.7, 1535.2, 1508.2 (s, C–C, phenyl); 952.8 (m, C=S). Elemental Anal. (%) Calc.: C, 51.7;H, 5.3; N, 20.1. Found: C, 51.2; H, 5.4; N, 19.8.

2.2.4. p-Hydroxybenzaldehyde thiosemicarbazone

IR data (KBr, cm⁻¹): 3465.8 (s, OH); 3365.6, 3122.5 (s, N–H, NH₂); 3210.8 (m, N–H, NH); 1606.6 (s, C=N); 1587.3, 1548.7, 1508.2 (s, C–C, phenyl); 958.6 (m, C=S). Elemental Anal. (%) Calc.: C, 49.2; H, 4.6; N, 21.5. Found: C, 49.5; H, 4.1; N, 21.8.

2.2.5. o-Hydroxybenzaldehyde thiosemicarbazone

IR data (KBr, cm⁻¹): 3445.5 (s, OH); 3324.0, 3142.7 (s, N–H, NH₂); 3177.4 (s, N–H, NH); 1615.2 (s, C=N); 1543.8, 1493.7 (s, C–C, phenyl); 1063.6 (s, C=S). Elemental Anal. (%) Calc.: C, 49.2; H, 4.6; N, 21.5. Found: C, 49.3; H, 5.0; N, 21.2.

2.3. Preparation of the complexes

The complexes were synthesized by reaction of corresponding thiosemicarbazones with acetone solution of acetone-ZDA in 40 °C. The products were purified by recrystallization from acetone- acetylacetone (2:1 volume ratio) (yields 50–60%).

2.3.1. p-Dimethylaminobenzaldehyde

thiosemicarbazone-ZDA (1)

IR data (KBr, cm⁻¹): 3431.1, 3147.6 (s, N–H, NH₂); 3263.3 (m, N–H, NH); 2989.5, 2960.5, 2918.1, 2850.6 (m, C–H, CH₃, CH); 1610.5 (s, C=N); 1591.2, 1562.2, 1519.8 (C–C, phenyl); 1180.4 (s, C–O); 1016.4 (m, C=S).¹H NMR (DMSO-d₆, 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). Elemental Anal. (%) Calc.: C, 49.2; H, 6.2; N, 11.5. Found: C, 50.4; H, 6.5; N, 11.9.

2.3.2. *p*-Hydroxy-o-methoxybenzaldehyde thiosemicarbazone-ZDA (2)

IR data (KBr, cm⁻¹): 3514.1 (s, OH); 3425.3, 3184.3 (s, N–H, NH₂); 3290.3 (m, N–H, NH); 2968.2, 2927.7 (w, C–H, CH₃, CH): 1587.3, 1523.7, 1460.0 (C–C, phenyl); 1271.0, 1199.6 (s, C–O); 927.7 (m, C=S).¹H NMR (DMSO-d₆, ppm): 1.8 (s, 12H); 3.8 (s, 3H); 5.2 (s, 2H); 6.7–6.8 (d, 1H); 7.0 (d, 1H); 7.4 (s, 1H); 7.9 (s, 1H); 8.0 (s, 2H); 9.3 (s, 1H); 11.2 (s, 1H). Elemental Anal.

Table 1

(%) Calc.: C, 46.5; H, 5.5; N, 8.5. Found: C, 46.0; H, 4.8; N, 8.2.

2.3.3. p-Methoxybenzaldehyde thiosemicarbazone-ZDA (3)

IR data (KBr, cm⁻¹): 3377.1, 3172.7 (s, N–H, NH₂); 3151.2 (m, N–H, NH); 2964.4, 2839.0 (m, C–H, CH₃, CH); 1608.5 (s, C=N); 1587.3, 1523.7, 1487.0 (C–C, phenyl); 1257.5, 1174.6 (s, C–O); 927.7 (s, C=S). ¹H NMR (DMSQ-d₆, ppm): 1.8 (s, 12H); 3.8 (s, 3H); 5.2 (s, 2H); 6.9, 7.0 (d, 2H); 7.6–7.7 (d, 2H); 7.9 (s, 2H), 8.0 (s, 1H); 11.2 (s, 1H). Elemental Anal. (%) Calc.: C, 48 1; H, 5.7; N, 8.8. Found: C, 48.8; H, 5.4; N, 8.3.

2.3.4. p-Hydroxybenzaldehyde thiosemicarbazone-ZDA (4)

IR data (KBr, cm⁻¹): 3416.2 (m, OH): 3392.0, 3115.5 (m, N–H NH₂); 3219.5 (s, N–H, NH); 2851.5, 2823.0 (w, C–H, CH₃, CH); 1642.6 (m, C= N); 1611.0, 1584.8, 1517.8, 1443.4 (C–C, phenyl); 1234.8, 1170.2 (s, C–O); 927.7 (s, C=S).¹H NMR (DMSO-d₆, ppm): 1.8 (s, 12H); 5.2 (s, 2H); 6.7–6.8 (s, 2H); 7.5–7.6 (d, 2H); 7.7 (s, 1H); 7.9 (s, 2H); 9.8 (s, 1H); 11.2 (s, 1H). Elemental Anal. (%) Calc.: C, 46.9; H, 5.5; N, 9.1. Found: C, 46.4; H, 5.3; N, 8.5.

2.3.5. o-Hydroxybenzaldehyde thiosemicarbazone-ZDA (5)

IR data (KBr, cm⁻¹): 3452.3 (m, OH); 3359.8, 3166.9 (m, N–H, NH₂): 3278.8 (m, N–H, NH); 2980.5, 2920.7 (w, C–H, CH₃ CH); 1606.6 (s, C= N); 1550.7, 1515.9, 1446.5 (C–C, phenyl); 1278.7, 1205.4, 1157.2 (m, C–O); 1043.4 (m, C=S).¹H NMR (DMSO-d₆, ppm): 1.8 (s, 12H); 5.2 (s, 2H); 6.7–6.9 (m, 2H): 7.0–7.2 (m, 3H); 8.2 (s, 2H); 8.4 (s, 1H); 9.8 (s, 1H); 11.3 (s, 1H). Elemental Anal. (%) Calc.: C, 46.9; H, 5.5; N, 9.1. Found: C, 47.3; H, 6.2; N, 9.3.

2.4. Calculation of the second-order NLO response

All calculations were performed on a PC Pentium III 750MHz. The all-valence ZINDO/S (intermediate neglect of differential overlap) method in HYPERCHEM 5.11 software package (Hypercube, Florida) [13] was employed to calculate electronic spectra. Details of the Z1NDO

Optical absorption maxima of the five complexes in solvents of different polarities

	λ_{\max} (nm)							
	Toluene	CHCl ₃	Ethyl acetate	CH ₃ OH	DMF			
1	365	364	361	362	361			
	281	282	282	305	308			
2	335	332	330	328	334			
	306	288	292	303	306			
3	331	327	325	319	326			
	287	310	305	306	306			
4	337	331	327	322	330			
	283	290	294	300	304			
5	354	350	354	367	382			
	288	286	271	270	276			

method for calculating electronic spectra and second-order molecular nonlinear optical properties can be found elsewhere [14]. The molecular hyperpolarizabilities were calculated using PM3 parameterization in MOPAC software package (7.0) [15]. 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 AM1 parameterization [16].

3. Results and discussion

The synthesis of the thiosemicarbazones can be monitored by IR spectrum to verify the disappearance of the carbonyl signals. Formation of the complexes also can be monitored by IR spectrum, in which the C=S signals had red shifts of about 20 cm⁻¹, and by appearance of the resonance peaks in 1.8 ppm (s, 12H) and 5.2 (s, 2H) in ¹H NMR spectra, which indicate the inclusion of acetylacetone.

state $(\Delta \mu \text{ in } D)$, and composition of the inst excited states					
Complex	λ_{\max}	F	$\Delta \mu$	Composition of Cl expansion ^f	
1 ^a	311	1.107	5.21	$-0.665x_{78-81}$	
	271	0.620	-1.69	$-0.508x_{80-85}$	
2 ^b	322	0.87	-2.22	$0.599x_{78-81}$	
	273	0.71	-2.25	$-0.480x_{80-85}+0.326x_{79-84}$	
3°	319	0.774	-3.37	$0.554x_{75-78}$	
	305	0.335	-3.14	$-0.374x_{77-78}$	
	273	0.715	-2.96	$-0.448x_{77-82}-0.323x_{78-81}$	
4 ^d	323	0.632	-3.55	$0.516x_{72-75}$	
	305	0.424	-3.38	$0.376x_{74-75} - 0.349x_{72-75}$	
	274	0.704	-3.27	$-0.437x_{74-79}$	
5 ^e	321	0.67	-4.51	$0.528x_{72-75}$	
	307	0.23	-2.42	$0.360x_{74-75}$	
	273	0.74	-4.48	$0.446x_{74-79}$	

ZINDO/S derived maximal absorption (λ_{max} in nm), oscillator strengths (*f*), dipole moment changes between ground state and excited state ($\Delta \mu$ in D), and composition of the first excited states

^a Orbital 80 is the HOMO, and 81 is the LUMO.

^b HOMO, 80; LUMO, 81.

Table 2

^c HOMO, 77; LUMO, 78.

^d HOMO, 74; LUMO, 75.

^e HOMO, 74; LUMO, 75.

^f Configuration interaction.

3.1. Solvatochromism and electronic spectra

The UV-vis absorption wavelengths of the complexes in some solvents of different polarities are listed in Table 1. It is obvious that all absorption maxima of the five complexes are located in UV region, which is in agreement with the colors of the five complexes listed in Table 3. All of the compounds exhibit solvatochromism, that is, their maximal absorption peaks show hypsochromic or bathochromic shifts with increasing solvent polarity. This means negative or positive dipole moment change between the ground and the excited state, respectively, and hence indicate obvious charge-transfer (CT) character for the associated optical transition. It is notable that all of the five complexes have two bands showing solvatochromism. It is well known that solvatochromism is based on Two-Level Model in which only HOMO and LUMO, i.e. ground and first excited-state, are involved in CT character, and is relatively valid in a large number of organic NLO chromophores. However, it is quite complicated in predicting the extent of the NLO properties of organometallic and coordination NLO materials, in which several optical transitions may be involved in the NLO response [17]. Anyway, it is reasonable to say that the solvatochromism in 1–5 indicates the change of the dipole moments in the ground and the excited states ($\Delta\mu$) which verifies the existence of intramolecular charge transfer.

The results of ZINDO/S calculation are listed in Table 2. The experimental optical spectra in relatively less polar chloroform solution and calculated ZINDO/S derived electronic spectrum of complexes 1 and 2 are compared in Fig. 1. The agreement between calculation and experiment is rather good, although there exist 10-40 nm error in λ_{max} between calculated and experimental data, which is within the error range of ZINDO/S calculation of some other types of complexes [17,18]. The results show all complexes have more than one maximal absorption peak. In the case of complex 1, there are mainly two absorption maxima at 311 nm (f = 1.107) and 271 nm (f =0.620). As for complex 2, they are at 322 nm (f =0.87) and 273 (f = 0.71).



Fig. 1. ZINDO/S derived electronic transitions of the complex 1 (top) and 2 (bottom) and their comparison with experimental data. The columns represent the oscillator strength (f) of the various transitions, while the curves represent the experimental optical spectrum.



3.2. Calculations of β values

MOPAC 97 software package has been used to calculate the β values of complexes 1–5 and their corresponding thiosemicarbazone ligands (Table 3). AM1 parameterization was utilized to optimize the structures of the five compounds and found that zinc, sulfur and four oxygens constitute square-pyramidal configuration (Fig. 2), which is consistent with the crystal structure of PZDA [10].

Table 3 The calculated β_0 and λ_{max} recorded in chloroform of the complexes and the corresponding thiosemicarbazone ligands

	β_0 (cal) (× 10 ⁻³⁰ (esu))		λ_{\max} (nm)	$\lambda_{\rm max}$ (nm)		Colors	
	Complex	Ligand	Complex	Ligand	Complex	Ligand	
1	30.6	21.5	364	365	Light yellow	Light yellow	
2	11.7	9.3	332	332	White	White	
3	12.4	9.8	327	326	White	White	
4	10.3	7.9	331	328	White	White	
5	7.8	4.9	350	337	White	White	

We can find that the calculated first molecular hyperpolarizabilities (β) of all of the five coordination compounds are larger than that of *p*-nitroaniline (6.8×10^{-30} esu, calculated value), among which complex **1** shows the largest β (39.1×10^{-30} esu). Comparing with their corresponding thiosemicarbazone ligands, the β values of the five coordination compounds also increase dramatically.

The experimental absorption maxima of longest wavelength of the complexes and their corresponding thiosemicarbazone ligands recorded in chloroform are listed in Table 3. It seems that the bands of the complexes do not show obvious red shifts comparing with their corresponding ligands. This is due to the d¹⁰ electron structure of Zn(II) ion, which makes it difficult to undergo intramolecular charge transfer process through metal ion. So we can infer that the zinc ion is hardly involved in the intramolecular CT process [9]. On the other hand, the metal complexation decreases the electron density of S atom (changed from 6.2420 to 6.1603 for 1, MOPAC calculated result), thus enhances the electron-acceptor effect of C=S group. This can be proven by the MOPAC calculated result of 1 that the electron density of the carbon atom of C=S group decreases from 4.1334 to 4.0330 upon complexation. This makes it easier to carry out the charge transfer from phenyl group to C=S group in thiosemicarbazone. This may be the reason that the first-order molecular hyperpolarizabilities of the complexes have increased comparing with the corresponding thiosemicarbazones, while the colors of the complexes are still the same as those of their ligands.

4. Conclusions

A new method aiming at suppressing so-called nonlinearity-transparency trade-off through coordination chemistry has been delivered on the basis of spectroscopic studies and first-order molecular hyperpolarizabilities analyses of a series of square-pyramidal coordination compounds. The involvements of Zn(II) ion with d^{10} electron structure and colorless thiosemicarbazones in the complexes result in obvious enhancements of the first-order molecular hyperpolarizabilities, comparing with their ligands, while the colors unchanged.

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