

# Crystal structures, molecular packing and picosecond optical limiting properties of quadridentate Schiff base divalent metal complexes derived from *S*-benzyl dithiocarbazate

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Received (in Montpellier, France) 31st January 2000, Accepted 17th March 2000

Published on the Web 20th April 2000

The neutral divalent metal complexes ML [ $H_2L = 1,4\text{-bis}(2'\text{-formylphenyl})\text{-}1,4\text{-dioxabutane bis}(S\text{-benzyl dithiocarbazate})$ ;  $M = Ni, Pd \text{ and } Zn$ ] show strikingly different crystal packing patterns. In NiL,  $C_{32}H_{28}O_2N_4S_4Ni$  the geometry around the metal atom is shown to be distorted square planar with a shortest  $Ni(1) \cdots S(1A)$  (etheral sulfur) contact of  $3.547(2) \text{ \AA}$  in neighboring molecules. The coordination configuration about PdL,  $C_{32}H_{28}O_2N_4S_4Pd$ , is square planar with a closest  $Pd(1) \cdots S(1A)$  (thiolato) contact of  $3.674(1) \text{ \AA}$  in neighboring molecules. The molecular packing of PdL in the unit cell is different from that of NiL, but like a previously reported structure of CuL. Unlike NiL and PdL the molecular structure of ZnL,  $C_{32}H_{28}O_2N_4S_4Zn$ , has a  $C_2$  crystallographic axis and the monomer is woven into a polymeric structure by weak intermolecular  $S(\text{thiolato}) \cdots H$  interactions of  $2.836 \text{ \AA}$ . The picosecond optical limiting properties of ML [ $M = Cu(II), Ni(II), Pd(II) \text{ and } Zn(II)$ ] were investigated. The limiting threshold for PdL is *ca.*  $0.9 \text{ J cm}^{-2}$ , comparable to that of  $C_{60}$  when an aperture is placed in front of the transmission detector, and *ca.*  $2.0 \text{ J cm}^{-2}$  without an aperture. The observed optical limiting effects are attributed to both nonlinear absorption and nonlinear refraction processes.

Optical limiting (OL) materials have been under intensive investigations because of their potential applications in the protection of optical sensors and human eyes from undesired intense laser beams.<sup>1</sup> An ideal optical limiter should have the capability of being transparent at low energy laser pulses and opaque at high energies. The most frequently reported materials are fullerene ( $C_{60}$ )<sup>2,3</sup> and metallophthalocyanine complexes,<sup>4,5</sup> which are considered as the best compounds for optical limiting; recently, inorganic clusters have also been investigated as promising optical limiting materials.<sup>6,7</sup> However, picosecond optical limiting materials have been less studied.<sup>8–12</sup> In a previous work, we have investigated nano- and picosecond optical limiting properties of the square planar Schiff base complex bis(*p*-nitrobenzaldehyde *S*-benzyl dithiocarbazate)copper(II).<sup>13</sup> In an attempt to seek new optical limiting materials among the  $\pi$ -electron delocalized systems containing mixed sulfur and nitrogen donors we report herein the picosecond optical limiting properties of the neutral divalent metal complexes  $ML_2[H_2L = 1,4\text{-bis}(2'\text{-formylphenyl})\text{-}1,4\text{-dioxabutane bis}(S\text{-benzyl dithio-carbazate})$  and  $M = Cu, Ni, Pd \text{ and } Zn$ ].<sup>14</sup> The picosecond limiting threshold for  $PdL_2$  is *ca.*  $0.9 \text{ J cm}^{-2}$ , which is comparable to that of  $C_{60}$  when an aperture is put in front of the transmission detector.

## Experimental

### Materials

All chemicals were reagent quality and used as received unless specifically noted. The solvents were purified by conventional

methods. The Schiff base ligand  $H_2L$  and its metal complexes CuL, NiL and ZnL were synthesized according to the procedure described earlier.<sup>14</sup>

### Synthesis of complex PdL

$PdCl_2$  (19.5 mg, 0.11 mmol) was dissolved in  $CH_3CN$  (10 ml) under reflux. This solution was added with  $H_2L$  (63 mg, 0.1 mmol) in DMSO (10 ml). After refluxing for 3 h, water was added to this clear solution to precipitate the product. The precipitate was thoroughly washed with hot ethanol and air dried to give pure product in 90% yield (72.7 mg). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a THF solution at room temperature. Anal. Calcd. for  $C_{32}H_{28}O_2N_4S_4Pd$ : C, 52.2; H, 3.8; N, 7.6. Found: C, 52.1; H, 3.3; N, 7.8%. IR:  $1485 \text{ cm}^{-1}$  (C=N). UV:  $\lambda/nm$  (log  $\epsilon$ ) 302 (4.51), 352 (4.39), 397 (4.03).

### Physical measurements

IR spectra were recorded on a Nicolet FT-IR-170SX instrument (KBr discs) in the  $4000\text{--}400 \text{ cm}^{-1}$  region. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. Electronic absorption spectra were obtained on a Shimadzu UV3100 spectrophotometer in dichloromethane solution ( $10^{-5} \text{ mol dm}^{-3}$ ).

### X-Ray crystallography

The relevant crystal data and structure parameters are summarized in Table 1. Suitable single crystals of NiL were

**Table 1** Crystal data for NiL, PdL and ZnL

	NiL	PdL	ZnL
Empirical formula	C <sub>32</sub> H <sub>28</sub> N <sub>4</sub> NiO <sub>2</sub> S <sub>4</sub>	C <sub>32</sub> H <sub>28</sub> N <sub>4</sub> PdO <sub>2</sub> S <sub>4</sub>	C <sub>32</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> S <sub>4</sub> Zn
Formula weight	687.53	735.22	694.19
Temperature/K	293(2)	293(2)	293(2)
Crystal system	P-1	P-1	pbcn
Space group	Triclinic	Triclinic	orthorhombic
<i>a</i> /Å	10.778(2)	10.7838(6)	4.6200(9)
<i>b</i> /Å	11.882(2)	11.1477(6)	20.561(4)
<i>c</i> /Å	13.830(2)	14.6503(8)	33.563(7)
$\alpha$ /°	81.079(13)	81.720(1)	90
$\beta$ /°	89.136(14)	84.405(1)	90
$\gamma$ /°	64.835(14)	66.350(1)	90
<i>U</i> /Å <sup>3</sup>	1581.1(4)	1594.9(2)	3188.2(11)
<i>Z</i>	2	2	4
$\mu$ /mm <sup>-1</sup>	0.914	0.880	1.069
Reflections collected	5742	10 318	14 700
Independent reflections	4996	7345	3217
<i>R</i> <sub>int</sub>	0.0342	0.0145	0.0672
Final <i>R</i> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0520, 0.1477	0.0354, 0.0806	0.0609, 0.1198
(all data)	0.0639, 0.1596	0.0458, 0.0861	0.1508, 0.1421

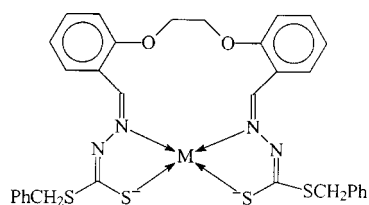
obtained by slow evaporation of a THF solution at room temperature. The intensities were collected using a Siemens P4 four-circle diffractometer with monochromated MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.<sup>15</sup> The structure was solved by direct methods. All computations were carried out on a PC-586 computer using the SHELXTL PC Program Package.<sup>16</sup>

The diffraction experiments on PdL and ZnL were carried out on a Siemens SMART CCD diffractometer with MoK $\alpha$  sealed tube at 293(2) K. For PdL the collected data were reduced by using the program SAINT<sup>17</sup> and an empirical absorption correction was done by using SADABS.<sup>18</sup> The structure was solved by direct methods using SHELXS86<sup>19</sup> and refined using SHELXTL96.<sup>20</sup> Needlelike single crystals of ZnL were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. Empirical absorption correction was applied to the data.<sup>21</sup> The structure was solved by direct methods and the computations were carried out using the SHELXTL 97 Program Package.<sup>22</sup>

All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were placed in their calculated positions (C–H, 0.96 Å) and assigned fixed isotropic thermal parameters. CCDC reference number 440/173. See <http://www.rsc.org/suppdata/nj/b0/b000960l/> for crystallographic files in .cif format.

## Results and discussion

Thiosemicarbazone-based ligands form stable metal complexes with a variety of transition metal ions. The Schiff base ligand H<sub>2</sub>L was doubly deprotonated on complexation with the divalent metal ions Ni(II), Cu(II), Pd(II) and Zn(II) forming stable neutral complexes ML (as shown in Scheme 1), which is evidenced from the absence of the characteristic  $\nu_{\text{NH}}$  at 3110 cm<sup>-1</sup> in the complexes.<sup>14</sup>



M = divalent metal ions, Co, Ni, Cu, Zn and Pd

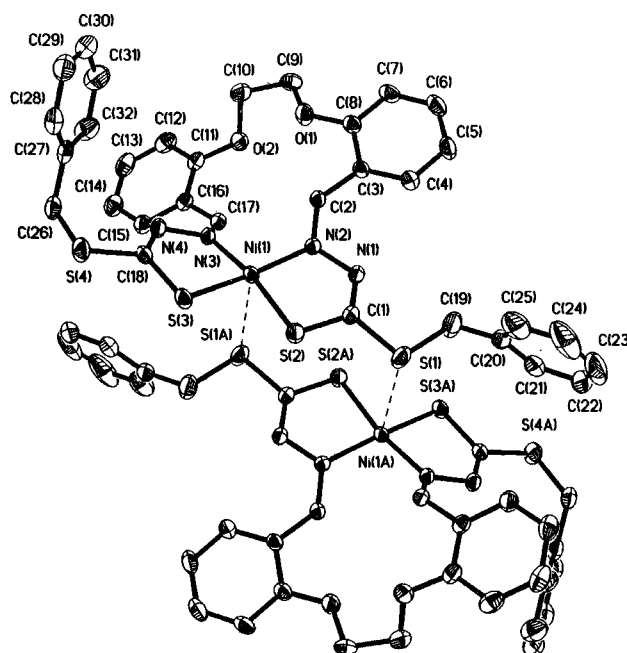
**Scheme 1**

## Single crystal structures

The molecular structures of NiL, PdL and ZnL are shown in Figs. 1–3 respectively. The bond lengths and angles are normal; selected bond lengths (Å) and angles (°) are listed in Table 2.

**NiL.** The coordination geometry of Ni(II) is distorted square planar [the dihedral angle between the chelate ring S(2)C(1)N(2)N(1)Ni(1) and its counterpart S(3)C(18)N(4)N(3)Ni(1) is 18.1°], similar to complex CuL,<sup>14</sup> due to their close effective ionic radius of about 0.63 Å.<sup>23</sup> The relatively small metal ionic radius fails to favor a normal square planar geometry when coordinated in a *cis* fashion to bring two bulky dithiocarbamate groups together.

**PdL.** The coordination geometry about Pd(II) is square planar [the mean deviation from the best plane N(1)N(2)S(1)S(2)Pd(1) is 0.0779 Å]. The larger effective ionic radius of Pd(II) of about 0.78 Å may be responsible for the better planarity, effectively bridging the two dithiocarbamate groups.<sup>23</sup>



**Fig. 1** Crystal structure of NiL.

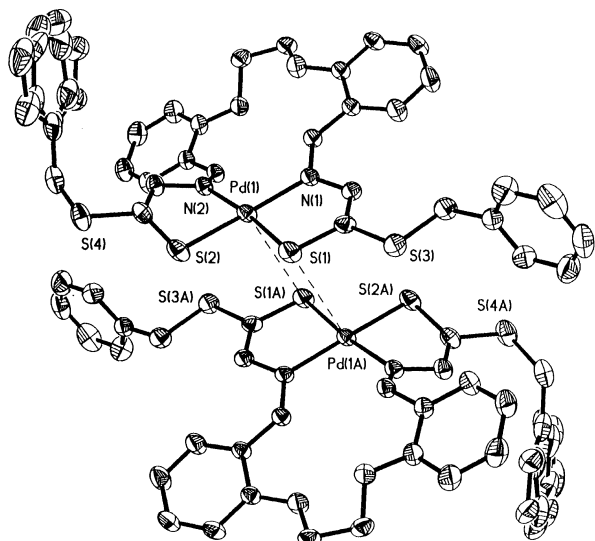


Fig. 2 Crystal structure of PdL showing disorder of one phenyl ring.

**ZnL.** The coordination configuration of Zn(II) is tetrahedral and has two equivalent N–Zn bonds of 2.048(4) Å and S–Zn bond of 2.2786(14) Å. The molecular structure has a  $C_2$  axis and the monomer is, in addition woven into a polymeric structure by weak intermolecular S(thiolato)···(H interactions of 2.836 Å, as shown in Fig. 3(b), which is shorter than the corresponding sum of van der Waals radii of 3.05 Å.

The divalent metal ions in ML [M = Ni, Cu, Pd and Zn] are four-coordinated, while in complex CoL<sup>24</sup> the Co(II) ion is in a distorted octahedral environment, coordinated by two  $\beta$ -nitrogens, two mercapto sulfur atoms and two ethereal oxygen donors from the doubly deprotonated Schiff base ligand. It is clearly shown that Co(II) exhibits a stronger affinity for oxygen donors than Cu(II), Ni(II), Pd(II) and Zn(II).

It is interesting to compare the molecular packing patterns of NiL, PdL and CuL. Because of the two preorganized bulky dithiocarbazate groups bridged by the  $-OCH_2CH_2O-$  group, the molecule is so congested that a centrosymmetric packing is adopted for all the three complexes to reduce steric hindrance in the unit cell.

The molecular packing of PdL is similar to that of CuL with a closest Pd(1)···S(1A) (thiolato) contact of 3.674(1) Å in two neighboring molecules, except that one phenyl ring in the two *S*-benzyl groups is disordered, which is ordered in CuL and NiL.

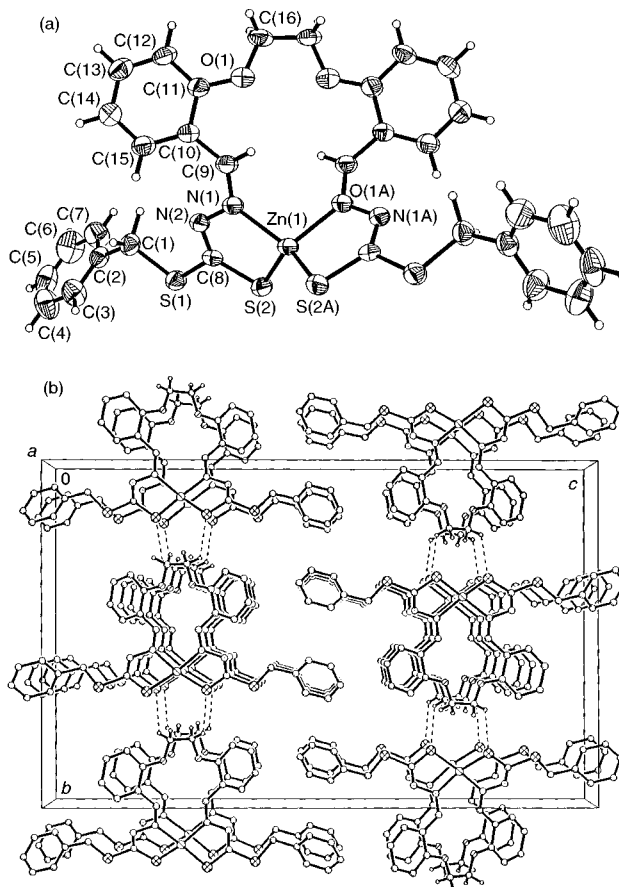


Fig. 3 (a) Crystal structure of ZnL; (b) the crystal packing of complex ZnL, showing the S(thiolato)···H (other hydrogens omitted for clarity).

The packing pattern of NiL is strikingly different from those of PdL and CuL, with a shortest Ni(1)···S(1A) (etheral sulfur) contact of 3.547(2) Å in two neighboring molecules. The difference apparently may be due to the facts that (i) Ni(II) has a  $d^8$  electronic configuration while Cu(II), has a  $d^9$  one; (ii) the effective ionic radius of Ni(II) is less than that of Pd(II) (the consequence is that Cu–S and Pd–S share similar bond lengths as well as Cu–N and Pd–N bonds in the complexes CuL and PdL).

#### Optical limiting properties

The electronic spectrum of PdL in  $CH_2Cl_2$  solution in the region of 250–500 nm is shown in Fig. 4. It is noted that for PdL, there is a relatively low linear absorption in the visible

Table 2 Selected bond lengths (Å) and angles (°) for NiL, PdL and ZnL

NiL			
Ni(1)–N(2)	1.910(3)	Ni(1)–N(3)	1.928(3)
Ni(1)–S(2)	2.1518(11)	Ni(1)–S(3)	2.1634(11)
N(2)–Ni(1)–N(3)	99.66(12)	N(2)–Ni(1)–S(2)	86.16(9)
N(3)–Ni(1)–S(2)	167.30(9)	N(2)–Ni(1)–S(3)	164.32(9)
Ni(1)···S(1A)	3.547(2)		
PdL			
Pd(1)–N(1)	2.079(2)	Pd(1)–N(2)	2.086(2)
Pd(1)–S(1)	2.2541(7)	Pd(1)–S(2)	2.2677(7)
N(1)–Pd(1)–N(2)	103.28(8)	N(1)–Pd(1)–S(1)	83.29(6)
N(2)–Pd(1)–S(1)	173.23(6)	N(1)–Pd(1)–S(2)	170.68(6)
Pd(1)···S(1A)	3.674(1)		
ZnL			
Zn(1)–N(1)	2.048(4)	Zn(1)–N(1)#1	2.048(4)
Zn(1)–S(2)	2.2786(14)	Zn(1)–S(2)#1	2.2786(14)
N(1)–Zn(1)–N(1)#1	105.8(2)	N(1)–Zn(1)–S(2)	86.22(12)
N(1)–Zn(1)–S(2)	131.31(13)	S(2)–Zn(1)–S(2)#1	120.96(7)

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

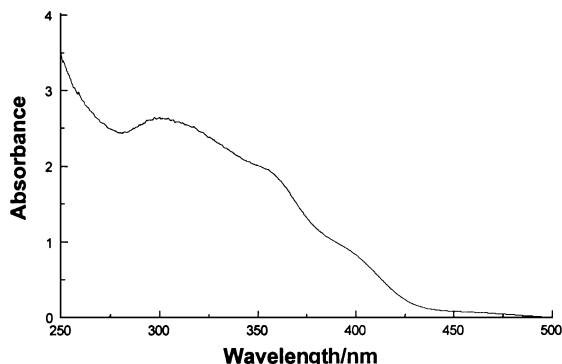


Fig. 4 The UV-Vis absorption spectrum of PdL in  $\text{CH}_2\text{Cl}_2$  solution.

and near-IR region. A broad transparent range is an important criterion in the assessment of optical limiting materials. A dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) solution of the complex was placed in a 1 mm thick quartz cell. The sample were irradiated by a frequency-doubled, mode-locked and Q-switched Nd:YAG laser, which produced linearly polarized 35 ps (FWHM) optical pulses at 532 nm for the picosecond optical limiting measurements. The laser was operated at a repetition rate of 10 Hz. The spatial profile of the optical pulses was nearly Gaussian after passing through a spatial filter. The pulses were split into two parts: the reflected one was used as a reference, while the transmitted one was focused onto the sample by using a 25 cm focal length mirror. The sample was placed at the focus where the spot radius of the pulses was deter-

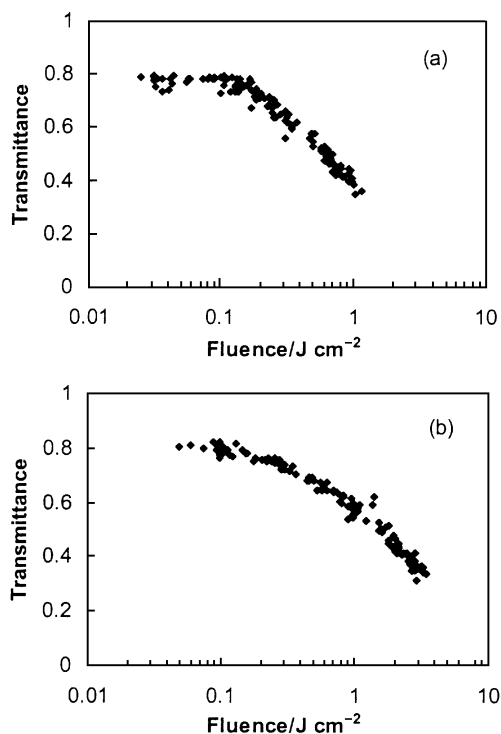


Fig. 5 Fluence-dependent transmittance of PdL in  $\text{CH}_2\text{Cl}_2$  solution measured with a pulse duration of 35 ps at 532 nm. Optical path: 1 mm. The measurement was performed: (a) with an aperture; (b) without an aperture.

Table 3 Optical data of CuL, NiL and PdL

	Limiting threshold/ $\text{J cm}^{-2}$		Effective nonlinear refraction coefficient $n_2/10^{-15} \text{ cm}^2 \text{ W}^{-1}$
	Closed aperture	Open aperture	
CuL	2	—	-1.6
NiL	2	—	-2.0
PdL	0.9	2	-2.8

mined to be  $24 \pm 5 \mu\text{m}$  by the Z-scan technique.<sup>25</sup> Both the incident and transmitted laser pulses were monitored simultaneously by using two energy detectors (RJP-735 energy probes, Laser Precision).

The optical limiting phenomenon was observed by measuring the nonlinear (energy-dependent) transmission. An aperture was placed in front of the transmission detector when the measurement was performed. Fig. 5(a) displays measurements of the optical limiting effect of PdL. The solution transmittance is independent of the incident fluence at  $<0.2 \text{ J cm}^{-2}$ , obeying Beer's law (the linear transmittance is about 80%). When the incident fluence exceeds  $0.2 \text{ J cm}^{-2}$ , the solution transmittance decreases rapidly as the incident fluence increases, thus exhibiting a typical optical limiting effect. The limiting threshold is defined as the incident fluence at which the solution transmittance falls to 50% of the linear transmittance. From Fig. 5(a), we determined the picosecond optical limiting threshold of PdL in  $\text{CH}_2\text{Cl}_2$  solution to be *ca.*  $0.9 \text{ J cm}^{-2}$ . The limiting thresholds for CuL and NiL measured under the same conditions are about  $2 \text{ J cm}^{-2}$ , while the solution transmittance of ZnL does not drop to 50% of the linear transmittance, due to its closed electronic valence shell.

Fig. 5(b) displays the optical limiting behavior of PdL at 532 nm when no aperture was placed in front of the transmission detector. The limiting effect is observed to deteriorate and the limiting threshold obtained is *ca.*  $2 \text{ J cm}^{-2}$  as in the case of CuL and NiL, the limiting thresholds cannot drop to 50% of the linear transmittance with no aperture.

The ML complexes are very stable and no photo-degradation occurs when the optical limiting measurements were performed at a repetition rate of 10 Hz. With an aperture placed before the transmission detector the optical limiting performance of the complexes ML is considerably enhanced. It is clearly demonstrated that a self-defocusing effect has enhanced the limiting behavior and that the observed optical limiting effect can be attributed to both nonlinear absorption and nonlinear refraction processes. The picosecond limiting threshold of  $0.9 \text{ J cm}^{-2}$  for PdL is comparable to that of  $\text{C}_{60}$  in toluene solution, which is considered as one of the best optical limiting materials.<sup>3</sup>

In our recent work, we have investigated the electron-donating [ $-\text{N}(\text{CH}_3)_2$ ] and withdrawing ( $-\text{NO}_2$ ) substituents on the nano- and picosecond optical limiting properties of the related square planar Schiff base complexes derived from *S*-benzyl dithiocarbazate.<sup>13</sup> It was found that the  $\text{NO}_2$ -containing complex exhibits lower optical limiting thresholds. The investigation of bis(*o*-bromobenzaldehyde *S*-methyl dithiocarbazate)Pt(II) (absence of disorder in the structure)<sup>26</sup> unfortunately shows that it behaves linearly when irradiated with 7 ns and 35 ps laser pulses at 532 nm. As seen from the  $n_2$  values in Table 3, PdL has a larger effective nonlinear coefficient than NiL and PdL. The disorder of one phenyl ring of the two *S*-benzyl rings in PdL may play an important role in its better optical limiting performance, compared to CuL and NiL in which no apparent disorder is found.

## Acknowledgements

This research was supported by the State Key Project of Fundamental Research, National Natural Science foundation of China and the National University of Singapore. Thanks go to Dr. Song-Ping Huang at Kent State University, USA for X-ray data collection on ZnL.

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