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Design, Synthesis, and Crystal Structure of a *cis*-Configuration N_2S_2-Coordinated Palladium(II) Complex: Role of the Intra- and Intermolecular Aromatic-Ring Stacking Interaction

Ze-Hua Liu, Chun-Ying Duan,* Jun Hu, and Xiao-Zeng You*

Coordination Chemistry Institute and The State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093, P. R. China

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A *cis*-configuration bis(4,5-diazafluorene-9-one thiosemicarbazone) palladium trihydrate, which exhibits approximately five times SHG (second harmonic generation) efficiency of urea, has been designed, synthesized, and structurally characterized. The complex, $C_{24}H_{16}N_{10}PdS_2\cdot 3H_2O$, crystallizes in trigonal space group $P3_1$ with cell parameters $a = 10.749(2)$ Å, $c = 19.872(4)$ Å, $V = 1988.3(6)$ Å^3, and $Z = 3$. The coordination geometry about the Pd(II) is surprisingly a *cis*-configuration square-planar formed by two imino nitrogen atoms N(3) and N(8) and two sulfur atoms S(1) and S(2) from two thiosemicarbazone ligands. Intramolecular contact analyses in the crystals and 1D and 2D ^{1}H NMR spectra in solution show that the *cis*-positioning of the two ligands was stabilized by the $\pi-\pi$ interaction between the two delocalized diazafluorene moieties. Detailed crystal structure analyses demonstrate that both the intermolecular $\pi-\pi$ stacking between the diazafluorene planes in different molecules and intermolecular hydrogen bonds between the water molecules and the deprotonated ligands might be the factors that influence the molecules to be packed in the acentric space group $P3_1$. The crystal structure of the free ligand was also reported here for comparison. The ligand, $C_{12}H_9N_5S$, crystallizes in orthorhombic space group *Pbca* with cell parameters $a = 8.432(2)$ Å, $b = 15.427(3)$ Å, $c = 17.387(3)$ Å, $V = 2272.7(8)$ Å^3, and $Z = 8$. The thiosemaicarbazone moiety adopts an *E* configuration with N(1) cis to N(3).

Introduction

There is currently active interest in the design of second-order NLO materials. Criteria have been discovered that are essential for exhibition of large hyperpolarizablities. The basic principles universally accepted are as follows:[1] (1) polarizable molecules with asymmetric charge distribution and a pathway of π-conjugated electrons; and (2) acentric crystal packing. Recently, tremendous effort has been devoted to design and synthesize new NLO materials of thiosemicarbazones and their metal complexes.[2−4] It has been postulated that the extensive electron delocalization in the thiosemicarbazone moiety is quite helpful for the free Schiff-base compounds and their metal complexes to show significant nonlinear optical properties.[5,6] However, experimental studies have been hampered by the inherent difficulty of designing a system in which high SHG efficiency can be exhibited, since in the presence of transition metal ions, the Schiff-base compound is rapidly converted into the *thiol* tautomeric form to facilitate the formation of centric neutral bis-ligand metal complexes.[7,8] To gain a better understanding of polarizable molecule in such systems, research has focused on the possible factors that influence the coordination geometry of the complex.[5,9,10]

Since the discovery in 1974 of intramolecular stacking interactions between the purine moiety of adenosine 5′-triphosphate and the aromatic ring 2,2′-bipyridyl in mixed ligand complexes,[11] various stacking interactions between suitable aromatic rings of two coordinated intramolecular ligands in ternary complexes have been investigated. These stacking interactions are especially fascinating due to their nature of biological molecular recognition and supramolecular interactions.[12,13] It has also been postulated the stacking interaction may influence the stability of the complex,[14,15] the UV charge-transfer bands,[16,17] the chemical shift in the ^{1}H NMR spectra,[18,19] as well as the rate of complex formation and the coordination geometry of the compounds.[20,21] In this paper, we design a

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thiosemicarbazone ligand with large π-system, 4,5-diazafluorene-9-one thiosemicarbazone and its palladium complex, bis(4,5-diazafluorene-9-one thiosemicarbazone)palladium. It can be expected that the intramolecular stacking interaction between the two extensive π systems of 4,5-diazafluorene rings can control the deprotonated ligands coordinated to palladium atom in an acentric *cis*-configuration, leading to the formation of a polarizable molecule. 1D and 2D ^1H NMR spectra of the complex in solution have been measured to study the solution structure and the possible intramolecular stacking in the solution.

Even if a molecule has a large hyperpolarizability value, it might fail to exhibit SHG activity, crystallization in a noncentrosymmetric space group must be also satisfied. About 70% of all chiral molecules crystallize in a centrosymmetric space group. To counter this, many strategies for forming acentric crystals capable of showing SHG activity have been employed, such as hydrogen bonding,[22−24] steric hindrance,[25] inclusion phenomena,[26−28] and cocrystallization.[29] These methods have met with varying degrees of success in ensuring a dipolar alignment that favors SHG. In this paper, we also discussed the influence of intermolecular aromatic ring stacking in the crystal packing. Least-squares planarity analysis and the atom−atom distances from the two pair of the diazafluorene moieties, as well as the atom−to−plane distances, indicate the presence of the strong intermolecular stacking. Hydrogen bond patterns are also discussed in order to determine the main factors that control the molecular packing.

Experimental Section

Materials and Measurements. Thiosemicarbazide and 4,5-diazafluorene-9-one (Aldrich) were used as received. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellet in the range 4000−400 cm^{-1}. Electronic absorption spectra were obtained on a Shimadzu UV-240 spectrophotometer in DMF solution (concentration of 1.0×10^{-4} M). 1D and 2D ^1H NMR spectra were recorded on AM5600 Bruker spectrometers in DMSO-d_6 solution at 298 K using TMS as internal standard.

Preparation of 4,5-Diazafluorene-9-one Thiosemicarbazone, HL. Five drops of acetic acid were added to a mixture of thiosemicarbazide (0.91 g, 10 mmol) and 4,5-diazafluorene-9-one (1.86 g, 10 mmol) in ethanol (30 mL). The resultant solution was heated to reflux for 3 h and on cooling, a yellowish white solid was formed and separated. Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution in air. ^1H NMR (DMSO-d_6, 298 K), δ (ppm), 8.873 (d, 1H, $J = 7.4$ Hz), 8.742 (d, 1H, $J = 7.5$ Hz), 8.638 (br, 1H, −NH), 8.543 (d, 1H, $J = 7.5$), 8.324 (d, 1H, $J = 7.5$); 8.15 (br, 2H, −NH$_2$), 7.574 (t, 1H, $J = 7.5$ Hz), 7.518 (t, 1H, $J = 7.5$ Hz). Anal. Calcd for $C_{12}H_9N_5S$: C, 56.2; H, 3.1; N, 27.1. Found: C, 56.4; H, 3.5; N, 27.4. IR (cm^{-1}, KBr disk), 3125 (br, ν_{N-H}), 1620, 1560 (s, $\nu_{C=N}$), 1491, 1392 (s, $\nu_{C=C}$), 1225 (s, ν_{N-N}), 1051 (s, $\nu_{C=S}$), 744 (s, δ_{C-H}).

Bis(4,5-diazafluorene-9-one thiosemicarbazone)palladium Trihydrate, PdL$_2$·3H$_2$O. Ethanol (20 mL) solution of the thiosemicarbazone (0.53 g, 2 mmol) and Pd(CH$_3$CN)$_2$Cl$_2$ (0.26 g, 1 mmol) were mixed together. The red crystalline solid formed after refluxing for 2 h was isolated and dried under vacuum. Crystals suitable for X-ray structure analyses were obtained by slowly evaporating a DMF solution in air. ^1H NMR, δ (ppm), 8.833 (d, 2H, $J = 8.1$ Hz), 8.528 (d, 2H, $J = 7.8$ Hz), 8.504 (d, 2H, $J = 4.7$ Hz), 8.178 (br, 4H), 7.952 (d, 2H, $J = 4.7$ Hz), 7.29 (q, 2H, $J = 7.6$ Hz), 6.935 (q, 2H, $J = 4.8$ Hz). Anal. Calcd for $C_{24}H_{16}N_{10}S_2Pd \cdot 3H_2O$: C, 43.5; H, 3.3; N, 20.9. Found: C, 43.8; H, 3.1; N, 21.4. IR (cm^{-1}, KBr disk), 1622, 1564 (s, $\nu_{C=N}$), 1458, 1400 (s, $\nu_{C=C}$), 1297 (s, ν_{N-N}), 1005 (s, ν_{C-S}), 748 (s, δ_{C-H}). Electronic spectra in DMF, λ_{max} ($\epsilon \times 10^3$, mol^{-1} L cm^{-1}): 373 (3.0) nm, 396 (3.1) nm, 438 (2.3) nm.

Crystallographic Analyses. Intensity data of HL were measured with a Rigaku RAxis-IIC imaging plate diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{max} = 55.0°$), with 40 oscillation frames and in the range of 0−180°, and exposure 10 min per frame.[30,31] Absorption corrections were made using the ABSCOR program based on Fourier-coefficient fitting to the intensities of symmetry-equivalent reflections.[32] Of 3673 reflections measured, 2567 were unique ($R_{int} = 0.012$) and used in the structure determination and refinement. Final cycles of refinement converged with discrepancy indices of $R = 0.041$ and $R_w = 0.086$. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were found from the differece Fourier map and refined isotropically.

Intensity data of PdL$_2$·3H$_2$O were measured on a Siemens P4 four-circle diffractometer with monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation using $\omega/2\theta$ scan mode with variable scan speed of 4.0−60.0° min^{-1} in ω. The data were corrected for Lorantz and polarization effects as well as for absorption, the maximum and minimum transmissions are 0.55 and 0.48, respectively, during data reduction using XSCANS.[33] Final cycles of refinement converged with discrepancy indices of $R = 0.062$ and $R_w = 0.085$.

The structures were solved by direct methods. All non-hydrogen atoms were refined anistropically by full-matrix least squares. Hydrogen atoms of the ligands were placed in their calculated positions with C−H = 0.96 Å, assigned fixed isotropic thermal parameters (1.2 times the atom to which they were attached), and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations. Hydrogen atoms of the water molecules in the complexes were located from the difference Fourier map and refined isotropically.

All computations were carried out on a PC-586 using the SHELXTL-PC program package.[34] Analytical expressions of neutral-atom scattering factors were employed, and anomalous disperion correctons were incorporated.[35] Details of crystal stucure determination of the free ligand and palladium complex are summarized in Table 1. Selected bond lengths and angles are listed in Table 2 for the free ligand HL and the palladium complex. Tables containing a full listing of atom positions, anisotropic displacement parameters, and hydrogen atom locations are available as Supporting Information.

Nonlinear Optical Property Measurement. The second-order nonlinear optical intensities are estimated by measuring the complex powder which diameters are from 76 to 154 μm in pellet with diameter as 10 mm. The thickness of each pellet is about 0.8 nm. The experimental arrangement for measuring the nonlinear optical properties utilizes an M200 high-power mode-locked Nd:YAG laser with 200 ps pulse at a repetition rate of 5 Hz. The selected wavelength is 1064 nm. After the selection of the wavelength, the laser beam is split into two

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Table 1. Details of Crystal Stucure Determination of the Free Ligand and Palladium Complex

	HL	$PdL_2 \cdot 3H_2O$
empirical formula	$C_{12}H_9N_5S$	$C_{24}H_{22}N_{10}O_3PdS_2$
fw	255.3	669.04
color	pale-yellow	red
cryst syst	orthorhombic	trigonal
space group	*Pbca*	$P3_1$
a	8.473(2) Å	10.749(2) Å
b	15.427(3) Å	10.749(2) Å
c	17.387(3) Å	19.872(4) Å
V	2272.7(8) Å^3	1988.3(6) Å^3
Z	8	3
d(calcd) (g cm^{-3})	1.492	1.676
μ (mm^{-1})	0.272	0.906
F(000)	1056	1014
temperature (K)	293	293
R^a	0.043	0.062
$R_w{}^b$	0.086^c	0.085^d

^{a} $R = \sum||F_o| - |F_c||/|F_o|$. ^{b} $R_w = [\sum w(|F_o{}^2| - |F_c|^2)^2/\sum w|F_o{}^2|^2]^{1/2}$. ^{c} $w^{-1} = \sigma^2(F_o{}^2) + (0.03P)^2 + 0.05P$, $P = [F_o{}^2 + 2F_c{}^2]/3$. ^{d} $w^{-1} = \sigma^2(F_o{}^2) + (0.07P)^2 + 0.15P$, $P = [F_o{}^2 + 2F_c{}^2]/3$.

parts: one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference (urea pellet). According to the principle proposed by Kurtz and Perry,[36] the SHG efficiency was estimated to be about 4.8 times that of urea. Although the palladium complex is red, there is no obvious absorption at 530 nm (ϵ at 530 nm is only 30 mol^{-1} L cm^{-1}).

Discussion and Results

The new Schiff-base HL was prepared by the reaction of thiosemicarbazide with the 4,5-diazafluorene-9-one in a 1:1 molar ratio. It can, in principle, exhibit thione−thiol tautomerism, since it contains a thioamide −HN−C═S functional group.[37,38] However the ν(S−H) band at 2570 cm^{-1} is absent from IR spectrum of the Schiff-base, but ν(N−H) at ca. 3130 cm^{-1} is present, indicating that the ligand in solid-state remains as the thione tautomer. The ^{1}H NMR spectrum in DMSO-d_6 does not show any peak at ca. 4.0 ppm attributing to the SH proton, suggesting that the thiol tautomeric form is absent even in solution. However, in the presence of Pd(II) ions, the Schiff-base compound is rapidly converted into the thiol tautomeric form to facilitate the formation of metal complex of the deprotonated ligand. A strong band at 1051 cm^{-1} in the IR spectrum of HL is assigned to ν(C═S). This band is red shifted ca. 50 cm^{-1} in the spectra of the Pd(II) complex. This observation can be explained by the exchange in the nature of the C═S bond on coordination of the ligand through the *thiol* form. The visible spectra are consistent with the structural formulas: the broad band at ca. 440 nm is assigned to the MLCT band of the palladium moiety, while the bands at 370 and 390 nm are assigned to the π−π* transition of the ligand.

Structure of Ligand HL. Figure 1 shows an ORTEP plot of the molecule with the atom numbering scheme. The thiosemicarbazone moiety shows an *E* configuration with N(1) cis to N(3) as found in most of the thiosemicarbazides[39−41] and thiosemicarbazones.[42−44] The C−S bond distance of 1.661(4) Å agrees very well with those in related compounds, being intermediate between 1.82 Å for a C−S single bond and 1.56 Å for a C═S double bond.[45] The corresponding C(1)−N(1) and C(1)−N(2) [1.306(5) and 1.381(5) Å] are indicative of some double-bond character. A comparison of the N(2)−N(3) of 1.354(4) Å with the corresponding distances of 1.411(2), 1.395(2), and 1.431(6) Å for unsubstituted thiosemicarbazide,[39] 1-phenyl,[40] and 4-phenyl[41] thiosemicarbazides, respectively, also suggests an extensive electron delocalization in the thiosemicarbazone. It can be said that this kind of electron structure is the main factor for the thiosemicarbazones showing quite large molecular hyperpolarizabilities.[3,4,46]

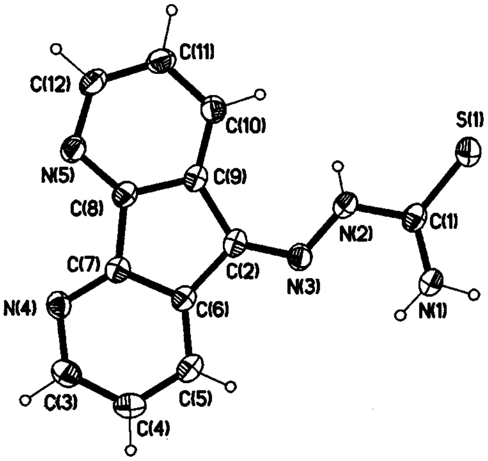

Figure 1. Molecular structure and atom numbering of the free ligand. The thermal ellipsoids are drawn at the 30% probability level.

The intermolecular hydrogen bonds which link the molecules together in the solid-state featured a infinite chain consolidated by hydrogen bonds of the type N(1)−H···N(4a) and N(1)−H···N(5a) (symmetry code a: −0.5 − *x*, 1 − *y*, −0.5 + *z*). The N···N distance of 3.076(6) and 2.945(5) Å for N(1)···N(4a) and N(1)···N(5a), respectively, agrees well with that of the NH_2···N(ring) distance reported by Fuller.[47]

Structure of the Pd(II) Complex. Figure 2 shows an ORTEP plot of the palladium(II) complex with the atom numbering scheme. The Pd(II) atom is coordinated in slightly distorted square-planar configuration with two Pd−N bonds and two Pd−S bonds. The mean deviations of PdSSNN coordination plane is ca. 0.033 Å. The ligand, like most of the thiosemicarbazones, loses a proton from the tautomeric *thiol* form and acts as a single negatively charged bidentate ligand coordinating to palladium ion via the mercapto sulfur and β-nitrogen atoms, forming a delocalized chelating plane.[48−50] The crowding between the two ligands in the complex is, however, relieved by the molecule assuming a *step* conformation,[51] which is

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Table 2. Selected Bond Lengthes (Å) and Angles (deg)

free ligand HL		palladium complex $PdL_2{\cdot}3H_2O$			
		Bond Lengths			
		Pd(1)−S(1)	2.241(1)	Pd(1)−S(2)	2.239(1)
		Pd(1)−N(3)	2.105(1)	Pd(1)−N(8)	2.117(2)
S(1)−C(1)	1.661(4)	S(1)−C(1)	1.768(2)	S(2)−C(13)	1.732(3)
C(1)−N(1)	1.306(5)	N(1)−C(1)	1.366(3)	N(6)−C(13)	1.331(3)
C(1)−N(2)	1.381(5)	N(2)−C(1)	1.323(2)	N(7)−C(13)	1.316(2)
N(2)−N(3)	1.359(4)	N(2)−N(3)	1.362(3)	N(7)−N(8)	1.367(2)
N(3)−C(2)	1.294(4)	N(3)−C(2)	1.309(2)	N(8)−C(14)	1.299(2)
		Bond Angles			
		N(3)−Pd(1)−S(1)	80.97(5)	N(8)−Pd(1)−S(2)	81.05(4)
		N(3)−Pd(1)−S(2)	172.82(5)	N(8)−Pd(1)−S(1)	172.93(4)
		N(3)−Pd(1)−N(8)	105.84(6)	S(2)−Pd(1)−S(1)	92.24(2)
N(1)−C(1)−S(1)	126.1(3)	N(1)−C(1)−S(1)	115.5(1)	N(6)−C(13)−S(2)	117.9(1)
N(2)−C(1)−S(1)	118.7(3)	N(2)−C(1)−S(1)	125.0(2)	N(7)−C(13)−S(2)	126.5(2)
N(1)−C(1) −N(2)	115.2(3)	N(1)−C(1)−N(2)	119.5(2)	N(6)−C(13)−N(7)	115.5(2)
C(1)−N(2)−N(3)	120.5(4)	C(1)−N(2)−N(3)	110.5(2)	C(13)−N(7)−N(8)	110.4(2)
N(2)−N(3)−C(2)	118.9(3)	N(2)−N(3)−C(2)	115.6(1)	N(7)−N(8)−C(14)	117.6(2)

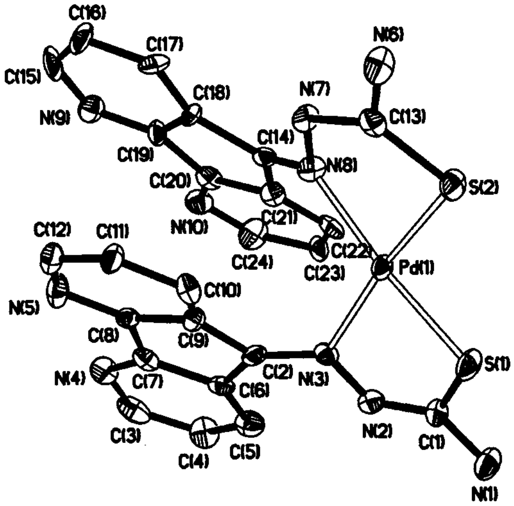

Figure 2. Molecular structure and atomic numbering of the palladium complex. The thermal ellipsoids are drawn at the 30% probability level.

characterized by the dihedral angles (ca. 31° in average) between the PdSSNN coordination plane and the two SCNN planes. This assumption is further supported by the small dihedral angle (ca. 3.6°) between the two SCNN planes. The most interesting structural feature of the complex is the surprising *cis*-configuration (N(3)−Pd−N(8) 105.8(1)°, S(1)−Pd−S(2), 92.2(1)°) with the two diazafluorene rings positioned on the same side. It is suggested that the *cis*-configuration is stabilized by the intramolecular stacking interaction between the two diazafluorene rings (Figure 3a). Least-squares planarity analysis shows that the two diazafluorene rings are almost parallel to each other (dihedral angle is 10.6°). The center-to-center separation between the two diazafluorene rings is ca. 3.18 Å, the smallest distance from an atom in one diazafluorene moiety to the mean plane of another stacking moiety is ca. 3.16 Å (Supporting Information), and the smallest interplane atom−atom distances is ca. 3.10 Å. This value is shorter than the 3.48 Å of the TCNQ complex and the 3.47 Å of the chlorine complex of MTDTPY,[52] 3.42 Å of the phen−phen distances in $[M(phen)_2][X_2]$ complexes,[51] 3.3−3.8 Å for several pyrene complexes,[53−55] and 3.40 Å of 2,7-bis(methylthio)-1,6-(dithiapyrene) (MTDTPY) radical salts from uniform columnar stacks.[56]

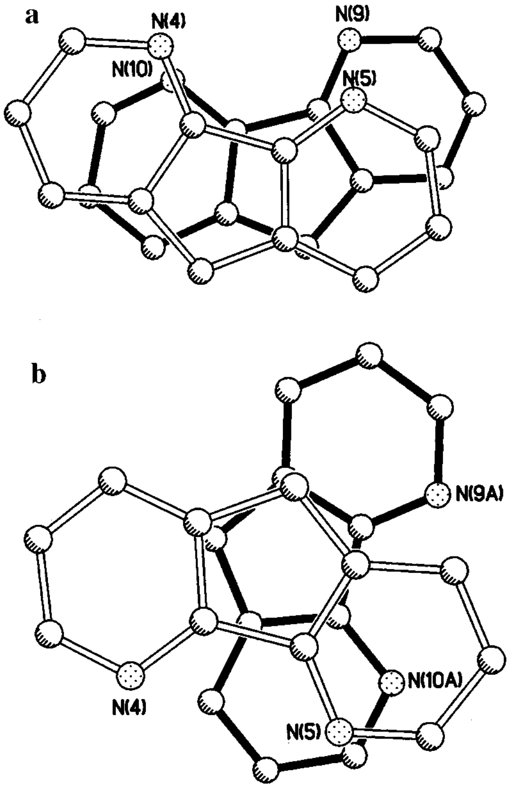

Figure 3. Diagram of the units in PdL_2, showing (a) intramolecular stacking and (b) intermolecular stacking. Symmetry code A: $-1 - x + y$, $-1 - x$, $-0.3333 + z$.

Solution Structure of the Palladium Complex. Both 1D and 2D ^{1}H NMR spectra of the complex also give direct evidence on the distance of hydrogen atoms in solution and determine accordingly the extent of stacking. The 2D COSY map of complex in DMSO-d_6 solution is shown in Figure 4a with the 1D ^{1}H NMR spectrum on the top. The broad peak which shows no hydrogen−hydrogen coupling was easily assigned as the

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proton attached to the amino nitrogen atom. In the upfield region, two protons at ca. 7.3 and 6.9 ppm might be assigned to the H_γ and $H_{\gamma'}$.[57] Considering the effect of nitrogen atom of Schiff-base, the chemical shift of H_γ should appear in the downfield region since the carbon atom that the proton attached is in the *cis*-position with respect to the imine nitrogen atoms. The other peaks are easily assigned from the COSY spectra, the peak ca. 8.0 ppm might be assigned as $H_{\beta'}$, and the peak at the most downfield region is the H_δ. The double peaks with chemical shifts 8.53 and 8.50 ppm are assigned as the protons of $H_{\delta'}$ and H_β, respectively. The values of coupling constants *J* are consistent with this assignment.

Detailed ^{1}H NMR studies of the ligand and the complex show that there are some significant upfield shift ($\Delta\delta$) of protons after the complex formation, as $\Delta\delta$ values are 0.21, 0.37, and 0.58 ppm for the protons of $H_{\delta'}$, $H_{\beta'}$, and $H_{\gamma'}$, respectively, while the protons attached to another pyridine ring do not show significant upfield shifts ($\Delta\delta$ < 0.05 ppm). Sigel[58,59] and Yamauchi[60,61] concluded that the upfield shifts might be contributed to the existence of intramolecular interaction due to the ring current effect of aromatic ring. The magnitude of the shift($\Delta\delta$) shows that there are intramolecular stacking interaction between the pyridine rings of the complex in solution.

Figure 4b shows the NOSEY spectrum of the complex. It is clear to see that there is a strong coupling between the H_δ proton in one ligand and the $H_{\beta'}$ proton in another ligand. The stronger cross-peak of two nonbonding hydrogen atoms shows that their separation is rather short in solution, and these results agree with those of X-ray crystal structure determination of the complex.

Molecular Packing in the Crystal. As shown in Figure 3b, the crystal is stabilized by the intermolecular stacking interaction. Least-squares planarity analysis shows that the two diazafluorene rings are almost parallel each other (dihedral angle is 1.4°). For these diazafluorene rings, the smallest intermolecular atom−atom distance is 3.40 Å and the smallest distance from an atom in one molecule to the mean plane defined by the diazafluorene ring in another molecule is 3.04 Å, indicating the strong intermolecular stacking interaction between the two ligands.

It is interesting to note that the intramolecular and intermolecular stacking between the two diazafluorene rings are different. The intramolecular stacking is shown in Figure 3a whereas the intermolecular stacking is shown as Figure 3b. The intermolecular stacking is a consequence of the 3_1 screw-axis in the $P3_1$ space group.

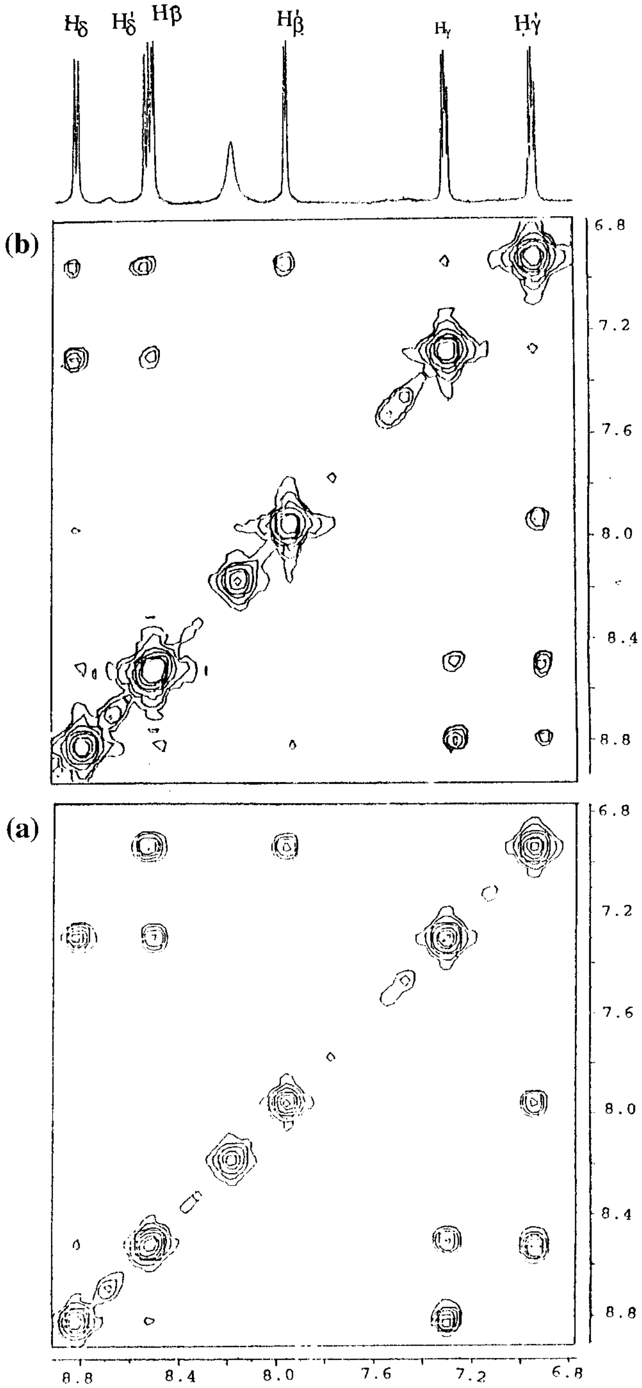

Figure 4. NMR spectrum of PdL_2 in DMSO-d_6 solution with TMS as internal standards at 298 K. The spectra were recorded on Bruker 500 MHz instruments. (a) COSY. (b) NOSEY.

It is also suggested that the crystal lattice is further stabilized by hydrogen bonding. There are six protons from the three water molecules and four protons from two primary amino nitrogen atoms having the potential to form donor hydrogen bonds. The most important hydrogen bonds are those that link the three water molecules to one another, O(1W)···O(3Wa) (symmetry code a: $1 - x + y$, $-1 - y$, $-0.3333 + z$), O(2W)···O(1W), O(3W)···O(2W), to form an infinite screw chain along the 3_1 axis (Figure 5). a similar structure has been reported in the molecular packing of phenanthroline monohydrate.[62] Molecules of the metal complex connected to the infinite hydrogen-bonded

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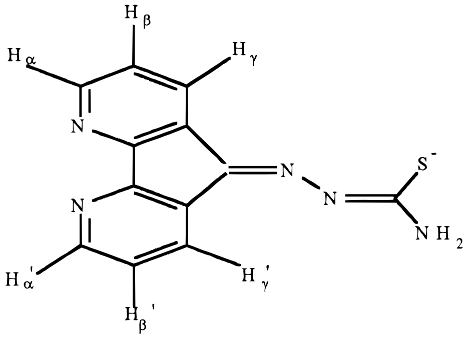
(57) The hydrogen atoms attached to the diazafluorene ring are defined as



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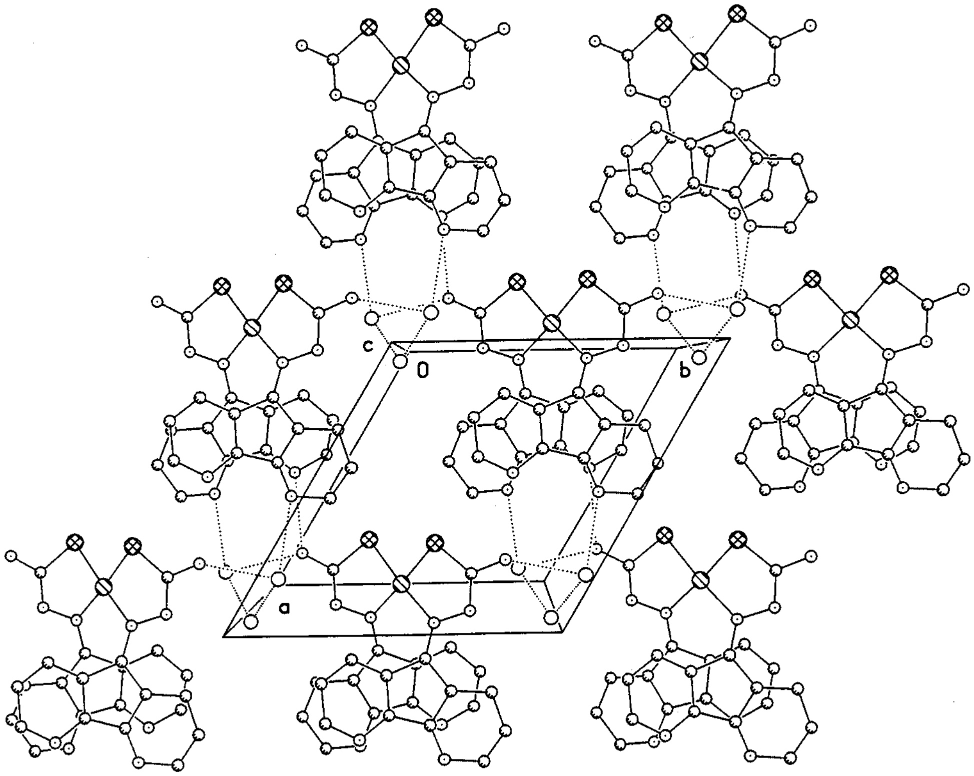

Figure 5. Hydrogen bonding scheme showing an infinite chain along the 3_1 axis.

Table 3. Inter- and Intramolecular Hydrogen Bond Lengths (Å) and Angles (deg)

D	H	A	D···A	H···A	D−H···A	symmetry code
O(1W)	H(1WB)	O(3Wa)	2.714(5)	2.10(3)	173(3)	a: $-1 - x + y$, $-1 - x$, $-0.3333 + z$
O(2W)	H(2WB)	O(1W)	2.792(5)	1.82(3)	168(2)	
O(3W)	H(3WB)	O(2W)	2.824(5)	2.28(2)	134(2)	
O(2W)	H(2WB)	O(1W)	2.966(6)	2.49(2)	137(3)	
O(2W)	H(2WB)	O(1W)	2.961(6)	2.28(2)	157(3)	
N(1)	H(1A)	O(1Wb)	2.920(6)	2.156(3)	147.82(7)	b: $1 + x, y, z$
N(1)	H(1A)	O(1Wb)	2.963(6)	2.107(2)	173.52(8)	
N(1)	H(1A)	O(1Wb)	2.991(6)	2.261(3)	142.61(7)	c: $1 + x, 1 + y, z$
N(6)	H(6B)	O(1Wb)	3.010(7)	2.155(2)	173.03(8)	

water chain through hydrogen bonds: O(1Wb)···N(1), O(1W)···N(4), O(3Wc)···N(6), O(3W)···N(9) (symmetry code b, $1 + x$, y, z; c, $1 + x$, $1 + y$, z) (Table 3). The other two hydrogen atoms with the N(1) and N(6) atoms are linked to the other pyridine nitrogen N(5) and N(10) through hydrogen bonds N(1)···N(5), N(6)···N(10), to form the two-dimensional hydrogen-bond system.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for HL and PdL·$3H_2O$ are available free of charge via the Internet at http://pubs.acs.org.

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