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ARTICLES

Photoinduced Intramolecular Proton Transfer of Phenol-Containing Ligands and Their Zinc Complexes

Helmut Görner,* Sumit Khanra, Thomas Weyhermüller, and Phalguni Chaudhuri*

Max-Planck-Institut für Bioanorganische Chemie, D-45413 Mülheim an der Ruhr, Germany

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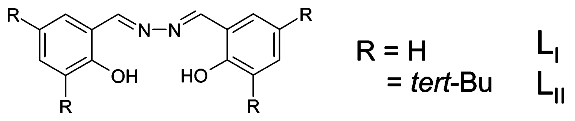
N,*N*′-Bis(salicylidene)hydrazine (L_I), a bis-2-hydroxybenzene-type ligand H_2L, its *tert*-butyl derivative (L_{II}), and the corresponding Zn^{2+} complexes of the type $Zn_2(LH)_2L$ (Zn−I and Zn−II) were synthesized. The molecular structure of Zn−II was determined by X-ray crystallography at −170 °C. The photoreactions of the four compounds in solution were studied by time-resolved UV−vis spectroscopy using nanosecond laser pulses. A weak but strongly Stokes shifted fluorescence signal of the ligands L_I or L_{II} is suggested to be due to excited-state intramolecular proton transfer (ESIPT) from the phenolic hydroxy group to the nitrogen of the methine bond in analogy to the fast enol → keto tautomerization of other 2-hydroxybenzenes. A transient with the maximum at 480 nm, bleaching at 370 nm, and a lifetime of 0.01−0.3 ms is attributed to the *trans*-keto tautomer, formed via internal conversion. The decay occurs via trans → cis isomerization and proton back-transfer to the enol form. Quenching by water indicates a proton-catalyzed reaction. To account for similar fluorescence and transient properties in the cases of the Zn^{2+} complexes, a photoinduced tautomerism at one of the two free phenolic hydroxy groups is proposed. The rapid ESIPT followed by a relatively slow relaxation process is reversible.

Introduction

Widespread occurrence of tyrosyl radicals in metalloproteins involved in oxygen-dependent enzymatic radical catalysis[1,2] has sparked and fueled the interest of chemists in using phenol-containing ligands to study model compounds that contain coordinated phenolate and its one-electron oxidized phenoxyl radical.[3] In a series of papers[4] we have already demonstrated the catalytic activity of phenol/phenoxyl-containing transition metal complexes for aerial oxidation of organic substrates such as alcohols, amines, and catechols; these are rare examples of functional models for metalloenzymes such as galactose oxidase, amine oxidases, and catechol oxidases. Additionally, one-electron oxidation of a hydrogen-bonded phenol can occur by concerted proton-coupled electron transfer.[5] We have prepared a phenol-containing ligand *N*,*N*′-bis(salicylidene)hydrazine (L_I), its *tert*-butyl derivative (L_{II}) and, because the Zn^{2+} ion is redox-inactive, their corresponding zinc complexes (Zn−I and Zn−II). It appeared attractive to examine the photochemistry of these ligands and complexes.



Details of a few photoreactions of Zn^{2+} complexes with phenolate ligands have been published.[6−10] The knowledge from radiation chemistry and the properties of the phenoxyl radicals in aqueous solutions have been summarized.[11] Photodeactivation of sterically hindered phenols occurs by internal conversion. From the effects of alkyl substitution of phenols, steric hindrance, solvent polarity and a balance of the deactivation channels of the first excited singlet state, Brede and co-workers have concluded that 2,6-di-*tert*-butylphenol is the most efficient light quencher.[12] The photochemistry of phenols has recently been reviewed.[13,14]

When an appropriate H-atom acceptor group is substituted in the ortho-position to a phenol, an intramolecular proton transfer may play a decisive role.[15−19] Some 2-hydroxyphenyl compounds exhibit strongly red-shifted fluorescence under conditions where hydrogen bonding of the phenolic hydroxyl group to a nearby nitrogen atom is possible. The reason for the large Stokes shift is excited-state intramolecular proton transfer (ESIPT), which converts the normal enol into the keto form. ESIPT has been documented for 2-(2′-hydroxyphenyl)benzoxazole (HBO), 2-(2′-hydroxyphenyl)benzothiazole (HBS), (2-hydroxyphenyl)benzazole, and various related 2-hydroxybenzenes.[15−29] The photoconversion of these model compounds from the enol form into the *cis*- and *trans*-keto forms was found to be extremely fast.[15]

Here, the photoreactions of the bis-salicylaldazine ligands L_I and L_{II} as well as two corresponding Zn^{2+} complexes were studied in solution by time-resolved UV−vis spectroscopy. The observed transient upon excitation at 308 nm is attributed to a *trans*-keto tautomer that is photochemically produced by intramolecular proton transfer from the hydroxy group to the

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* Corresponding authors. E-mail: H.G., goerner@mpi-muelheim.mpg.de; P.C., chaudhuri@mpi-muelheim.mpg.de.

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nitrogen of the methine bond. The decay properties via the *cis*-keto to the enol form were compared with those of HBO and HBS.

Experimental Section

Synthesis of L_I was analogous to that described elsewhere.[30] Synthesis of L_{II} was as follows: 3,5-Di-*tert*-butylsalicylaldehyde (2.34 gm, 10 mmol) and hydrazine hydrate (0.24 mL, 5 mmol) were dissolved in 30 mL of methanol to yield a yellowish clear solution, which was refluxed for 30 min. The resulting precipitate was yellow microcrystalline solid. This was filtered, washed with hexane, and then air-dried. The ligand was recrystallized from dichloromethane solution. Yield: 180 mg (70%). Anal. Calcd for $C_{30}H_{42}N_2O_2$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.8; H, 9.1; N, 6.1. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 1.34 (18H, s, t-Bu), 1.46 (18H, s, t-Bu), 7.19 (2H, s, Ar), 7.46 (2H, s, Ar), 8.76 (2H, s, azomethine), 11.86 (2H, s, OH-phenol). IR (KBr, cm^{-1}): 3448, 2959, 2869, 1623, 1591, 1456, 1438, 1250, 1229, 1172, 1025, 963, 715. ESI-MS (*m*/*z*): 464.

Synthesis of Zn−I was carried out using the same protocol as that for Zn−II, which is as follows: Bis-salicylaldazine ligand (LH_2) (0.23 gm, 0.5 mmol) was dissolved in CH_2Cl_2 (15 mL). Then a 15 mL methanol solution of 0.13 g of $Zn(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol) was added to the ligand solution, followed by Et_3N (0.13 mL, 1 mmol). The resulting solution was refluxed for 30 min under argon, and after cooling, a deep yellow microcrystalline solid precipitated out. This was filtered, washed with diethyl ether, and then air-dried. Suitable X-ray quality single crystals were grown from $CH_2Cl_2-CH_3CN$ solution of the complex. Yield: 145 mg (40%). Anal. Calcd for $C_{91}H_{131}N_6O_6Cl_2Zn_2$: C, 68.02; H, 8.22; N, 5.23; Zn, 8.14. Found: C, 68.7; H, 8.2; N, 5.2; Zn, 8.2. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 1.34 (54H, s, t-Bu), 1.46 (54H, s, t-Bu), 7.19 (6H, s, Ar), 7.47 (6H, s, Ar), 8.37(2H, s, azomethine), 8.50 (2H, s, azomethine), 8.79 (2H, d, azomethine), 11.86 (2H, s, OH-phenol). IR (KBr, cm^{-1}): 3448, 2956, 2906, 1614,1591, 1529, 1461, 1426, 1250, 1229, 1166, 1026, ESI-MS (*m*/*z*): 1057 $[L(LH)(Zn^{2+})_2]^+$, 1520 $[(Zn^{2+})_2L(LH)_2 \cdot CH_2Cl_2]^+$.

In the Zn−II complex 6-aldimine protons (HC═N resonance) are observed in the range 8.37−8.79 ppm, both as singlets and as doublets. The ^{1}H NMR spectrum clearly shows three different sets of aldimine protons at 8.37, 8.50, and 8.79 ppm with distinctly different chemical environments, in accordance with the X-ray structure. When the imine carbon carries one proton, the spectrum clearly shows hyperfine splitting of the imine protons due to coupling with the proton on nitrogen, which is also evidenced in the X-ray structure by the presence of strong hydrogen bonding of the phenolic group with the nitrogen. The downfield shift of the aldimine protons due to complexation is consistent with the literature values reported earlier.[30] We have measured temperature-dependent ^{1}H NMR spectra of the Zn−II complex in dichlomethane solution from +25 to −75 °C with a 10 deg interval, and they were found to be consistent in the said temperature range. The complex is fairly stable for at least 24 h. (We note that there is a possibility of the self-exchange-equilibrium, e.g., between a 2:1 complex and free ligand, as we have seen with prolonged time only a singlet of the aldimine protons in the ^{1}H NMR spectra). The appearance of intramolecular H-bonded phenolic protons at δ 11.86 ppm is consistent with the H-bonded phenolic protons shift in the case of the free ligands.

TABLE 1: Crystal Data and Structure Refinement for Zn−II

empirical formula	$C_{91}H_{130}N_6O_6Cl_2Zn_2$
formula weight	1605.65
temperature (K)	100(2)
wavelength (Å)	0.710 73
crystal system	monoclinic
space group	$P2_1/c$, No. 14
unit cell dimensions	
a (Å)	17.4953(9)
b (Å)	17.5283(9)
c (Å)	30.010(2)
β (deg)	96.766(5)
volume (Å^3); Z	9138.9(9); 4
density (cal) (Mg/m^3)	1.167
absorp coeff (mm^{-1})	0.635
F(000)	3440
crystal size (mm^3)	0.14 × 0.13 × 0.04
θ range for data collection (deg)	2.97−22.50
reflections collected	80163
independent reflections	11916 [*R*(int) = 0.0894)]
absorption correction	Gaussian, face indexed
data/restraints/parameters	11916/37/989
goodness-of-fit on F^2	1.166
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0814, wR2 = 0.1664
R indices (all data)	R1 = 0.0999, wR2 = 0.1744

The other compounds, HBO and HBS (Aldrich), and the solvents (Merck, Fluka) were used as received, e.g., acetonitrile (Uvasol quality) or methylcyclohexane (MCH) purified by distillation. The absorption spectra were monitored on a UV/vis spectrophotometer (HP, 8453). The molar absorption coefficients of L_I, L_{II}, and Zn−I in MCH are $\epsilon_{293} = 3 \times 10^4$, $\epsilon_{294} = 5 \times 10^4$, and $\epsilon_{305} = 9 \times 10^4$ M^{-1} cm^{-1}, respectively. An excimer laser (Lambda Physik, EMG 200) with a pulse width of 20 ns and an energy <100 mJ was used for excitation at 308 nm. For a few experiments $\lambda_{exc} = 248$ nm was used. As a measure of the yield, $\Phi\epsilon$ was determined for optically matched solutions using the TT absorption of benzophenone in acetonitrile at 525 nm, $\Phi\epsilon_{525} = 6 \times 10^3$ M^{-1} cm^{-1}. The IR difference spectra were recorded in a 0.5 mm CaF_2 cell on a FTIR spectrometer (Bruker IFS66). For excitation, another excimer laser (Radiant Dyes, EXC-100) was applied. The emission spectra were measured on a spectrofluorometer (Eclipse, Cary). The fluorescence excitation spectra of the ligands and complexes are similar to their absorption spectra concerning the long wavelength band. The fluorescence excitation spectra of the ligands and complexes deviate slightly from the absorption spectra in the shorter-wavelength region, e.g., when the samples are not diluted enough. The fluorescence lifetimes (τ_f) were determined from decay kinetics by a single-photon counting fluorometer (Edinburgh Instr. F900). The quantum yield of fluorescence (Φ_f) was determined using 9,10-diphenylanthracene in deoxygenated ethanol as reference, $\Phi_f = 0.9$. Irradiation was performed using the 366 nm line of a 1000 W Xe−Hg lamp and a monochromator. Photolysis of L_{II} or Zn−II in acetonitrile by 366 nm irradiation does not cause discernible absorption changes, in contrast to the complexes in dichloromethane, where decomposition was observed.

The crystallographic data for Zn−II are summarized in Table 1. Graphite monochromatic Mo Kα radiation, $\lambda = 0.710\ 73$ Å was used for Zn−II. Yellow crystals of Zn−II were fixed with perfluoropolyether onto glass fibers and mounted on a Nonius Kappa-CCD diffractometer equipped with a cryogenic nitrogen cold stream, and intensity data were collected at −173 °C. Final cell constants were obtained from a least-squares fit of the setting angles of all integrated reflections. Intensity data were corrected for Lorentz and polarization effects. The data set for Zn−II was corrected for absorption. The Siemens SHELXTL software package (G. M. Sheldrick, Universität Göttingen) was used for solution refinement and artwork of the structures; the neutral atom scattering factors of the program were used.

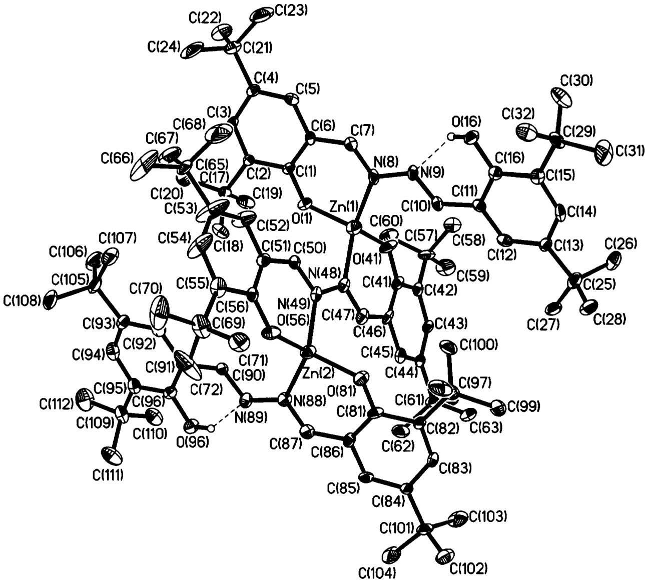


Figure 1. ORTEP view of the Zn−II complex.

TABLE 2: Selected Bond Lengths (Å) and Angles (deg) for Zn−II

Zn(1)⋯Zn(2)	5.06		
Zn(1)−O(41)	1.874(4)	Zn(2)−O(56)	1.879(4)
Zn(1)−O(1)	1.873(4)	Zn(2)−O(81)	1.885(4)
Zn(1)−N(8)	2.044(5)	Zn(2)−N(88)	2.023(4)
Zn(1)−N(48)	2.075(5)	Zn(2)−O(49)	2.036(5)
O(41)−Zn(1)−O(1)	122.4(17)	O(56)−Zn(2)−O(81)	124.11(17)
N(8)−Zn(1)−N(48)	123.36(18)	N(88)−Zn(2)−N(49)	118.78(18)
O(41)−Zn(1)−N(8)	115.94(19)	O(56)−Zn(2)−N(88)	114.21(18)
O(1)−Zn(1)−N(8)	93.79(17)	O(81)−Zn(2)−N(88)	95.45(18)
O(41)−Zn(1)−N(48)	93.90(18)	O(56)−Zn(2)−N(49)	95.89(17)
O(11)−Zn(1)−N(48)	109.79(17)	O(81)−Zn(2)−N(49)	110.18(18)

Results

Solid-State Structure of Zn−II. The molecular geometry and atom labeling scheme of the neutral molecule in Zn−II are shown in Figure 1. The structure of the complex molecule consists of a discrete neutral dinuclear unit and one dichloromethane molecule as solvent of crystallization. Selected bond lengths and angles are listed in Table 2. The X-ray structure confirms that a dinuclear Zn^{2+} complex has indeed been formed in such a way that the distorted tetrahedral geometry for each Zn^{2+} metal ion in the molecule is present. Each ligand binds two Zn metal atoms on each side of the N−N bond via one phenolate-O and one imine-N atom. The second ligand binds similarly, thus leaving one of the phenolate-O atoms, O(16) and O(96), in each of these two ligands protonated.

The short O(16)⋯N(9) and O(96)⋯N(89) separations of 2.617 and 2.628 Å, respectively, clearly indicate the occurrence of strong hydrogen bond interactions, shown by dotted lines in Figure 1, between the said atoms, suggesting protonated uncoordinated O(16) and O(96). Indeed, a difference Fourier analysis in the latter refinement stages did reveal peaks assignable to protons, and they were included in the final refinement cycle. The presence of two protons per dinuclear unit is in complete accord with the charge balance considerations of the neutral complex Zn−II. Thus the tetracoordinated metal ions have N_2O_2 coordination spheres with the salicylaldimine moiety in the facial mode with the Zn⋯Zn separation of ca. 5.06 Å. All the salicylaldimine fragments are satisfactorily planar. To accommodate two Zn ions, one of the ligands is twisted along the N−N bond. Large distortions from the ZnN_2O_2 tetrahedra are clearly evident, particularly from the bond lengths and angles. Such distortions are most probably due to the steric requirements of the dinucleating ligand. The average Zn−O bond length is around 1.875 Å, whereas the average Zn−N bond distance is 2.045 Å. The average trans O−Zn−O bond angle is 123.3°, whereas the trans N−Zn−N angle is 121.1°. Furthermore, the O−Zn−N angle lies in the range between 93.8° and 114.2°. Recently, dinuclear Fe^{3+} and Ru^{3+} complexes with the unsubstituted ligand have been reported.[32]

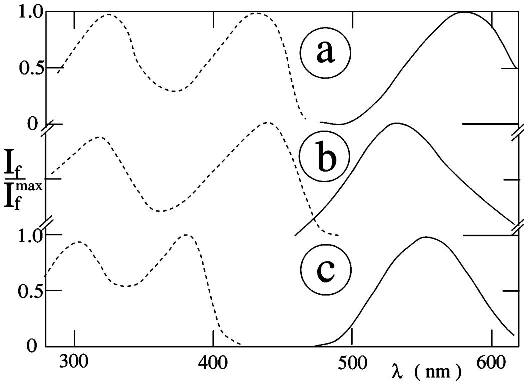


Figure 2. Fluorescence emission (right, $\lambda_{exc} = 380$ nm) and excitation (left, $\lambda_{em} = 550$ nm) spectra of (a) Zn−II, (b) Zn−I, and (c) L_I in MCH at 25 °C.

Ground-State Properties in Solution. The ligand L_{II} in cyclohexane at room temperature has an absorption spectrum with peaks at 290 and 360 nm, but no band above 400 nm. This is similar for both ligands in acetonitrile. The absorption spectrum of the complex Zn−II in cyclohexane has peaks at 310, 380 and 440 nm. Thermally, the absorption at 310 and 380 nm increases slightly with time and the 440 nm band decreases. The spectrum is initially also the same in carbon tetrachloride or dichloromethane, but the peak at 440 nm disappears faster, the half-life is a few hours. Zn−II in acetonitrile shows two peaks at 310 and 380 nm, no band above 400 nm and no thermal change. The 440 nm band of complex Zn−I also remains unchanged in acetonitrile or ethanol, in contrast to Zn−II. The stable complex in the cases of Zn−I in any solvent and of Zn−II in nonpolar solvents is due a to metal to ligand charge transfer (CT). For Zn−II in dichloromethane or solvents of larger polarity, we propose replacement of one ligand by these solvents and/or water. No spectral change was found for L_{II} in ethanol on addition of water (1−30%).

Fluorescence Properties. The emission of a complex in cyclohexane or MCH ($\lambda_{exc} = 360$ or 440 nm) shows a broad spectrum with maximum at $\lambda_f^{em} = 580$ nm for Zn−II (Figure 2a) and at $\lambda_f^{em} = 530$ nm for Zn−I (Figure 2b). The lifetime (τ_f) is shorter than 0.3 ns for the main component. Therefore, phosphorescence is excluded and the emission is attributed to fluorescence. An example of the fluorescence emission and excitation spectra is shown for L_I in MCH (Figure 2c). The fluorescence excitation spectra of the ligands and complexes in MCH, acetonitrile or ethanol are similar to their absorption spectra concerning the long wavelength band. Therefore, in the cases of the complexes, a CT to metal transition as the possible origin of the fluorescence can be excluded. Oxygen does not markedly change the emission intensity, which goes along with the relatively short fluorescence lifetime. Addition of water (0.01−1 M) to L_{II} in ethanol has only a minor effect.

The fluorescence at room temperature is generally weaker for the ligands than for the complexes. The quantum yields are between $\Phi_f = 0.003$ and 0.02 (Table 3). For HBO or HBS in acetonitrile the values are, to a certain extent, comparable, e.g., $\lambda_f^{em} = 500$ and 520 nm and $\Phi_f = 0.012$ and 0.015, respectively.

TABLE 3: Fluorescence Maxima and Quantum Yield of the Ligands and Complexes[a]

compd	solvent	λ_f^{ex} (nm)	λ_f^{em} (nm)	Φ_f
L_I	MCH	310, 380	550	0.001 (0.15)[b]
	acetonitrile	300, 380	550	0.0003
	ethanol	300, 390	550	0.0004 (0.2)
L_{II}	MCH	300, 380	560 (550)[b]	0.001 (0.12)
	acetonitrile	300, 380	540	0.0005
	ethanol	300, 370	550	0.0004 (0.18)
Zn−I	MCH	320, 440	530 (530)	0.002 (0.17)
	acetonitrile	320, 420	530	0.02
	ethanol	320, 420	520 (530)	0.005 (0.15)
Zn−II	MCH	320, 440	580 (540)	0.001 (0.14)
	acetonitrile	320, 430	570	0.003
	ethanol	320, 430	570	0.003 (0.16)

[a] Using $\lambda_{exc} = 380$ nm and $\lambda_{em} = 550$ nm at 25 °C. [b] Values in parentheses refer to −196 °C.

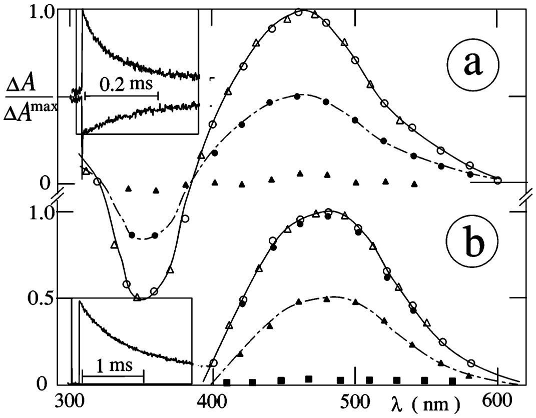


Figure 3. Transient absorption spectra of Zn−II in (a) MCH and (b) acetonitrile at 20 ns (○), 1 μs (△), 0.1 ms (●), 1 ms (▲), and 10 ms (■) after the 308 nm pulse. Insets: decay at 460 nm (upper) and 370 nm (lower).

The fluorescence intensity strongly increases on going to rigid media: $\Phi_f = 0.1-0.2$ for Zn−I or Zn−II in glassy MCH or ethanol at −196 °C (Table 3). The lifetime also increases, $\tau_f = 3-5$ ns at −196 °C, whereas the spectra have comparable band maxima (λ_f^{ex} and λ_f^{em}) for the ligands and complexes in fluid and glassy media.

TABLE 4: Transient Properties of the Ligands and Complexes[a]

parameter	solvent	L_I	L_{II}	Zn−I	Zn−II	HBS
λ_a (nm)	MCH	480	480	480	470	
	acetonitrile	480	480	480	480	430 [440][b]
	ethanol	480	480	480	490	
λ_b (nm)	acetonitrile	370	370	370	375	
yield[c]	acetonitrile	0.4	0.4	0.6	0.6	
k_w (10^5 $M^{-1}s^{-1}$)	*tert*-butanol	1.5	2	1.2	0.3	
	acetonitrile	0.5	0.4	0.8	0.5	0.2 [0.1]
	ethanol	1.8	1.6	1.4	0.1	

[a] In argon- or air-saturated solution at 25 °C, $\lambda_{exc} = 308$ nm. [b] Values in brackets refer to HBO. [c] Relative value $\Phi\epsilon/(\Phi\epsilon)_{ref}$ using benzophenone in acetonitrile as reference.

TABLE 5: Lifetime τ_K (μs) of the Keto Tautomer of the Ligands and Complexes[a]

solvent	L_I	L_{II}	Zn−I	Zn−II	HBS
cyclohexane/MCH	15	10	30	120	
dichloromethane[b]	100	60	50	200	
tert-butanol	20	30	10	300	
+water[b]	1.6	1	1.6	6	
acetonitrile	150	120	300	1200	30 [1][c]
+water[b]	1.2	1			
ethanol	16	15	20	60	80
+water[b]	1.5	1			

[a] In argon- or air-saturated solution at 25 °C, $\lambda_{exc} = 308$ nm. [b] In the presence of 5 M H_2O. [c] Value refers to HBO.

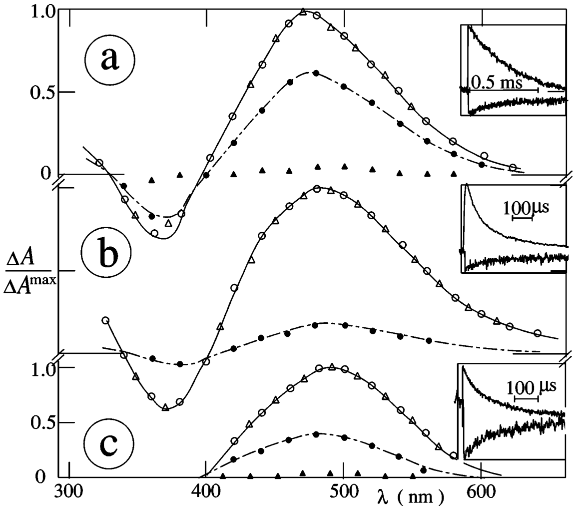


Figure 4. Transient absorption spectra of (a) Zn−I, (b) L_{II}, and (c) L_I in acetonitrile at 20 ns (○), 1 μs (△), 0.1 ms (●), and 1 ms (▲) after the 308 nm pulse. Insets: decay at 480 nm (upper) and 370 nm (lower).

Transient Absorption Properties. Transients were observed (within the excitation pulse) for the four compounds at ambient temperatures in all solvents examined. The transient of Zn−II in MCH (Figure 3a), acetonitrile (Figure 3b) or ethanol shows a broad absorption spectrum with a maximum (λ_a) at 480 nm and a bleaching (λ_b) at 370 nm, $\lambda_{exc} = 248$ nm. The transient absorption is similar, when Zn−II is excited at 308 nm, but the bleaching appears only at a sufficiently low concentration, e.g., corresponding to $A_{350} < 1$. The decay at 480 nm follows first-order kinetics at lower laser intensity and matches the bleaching recovery (inset of Figure 3a). The time-resolved UV−vis spectra of Zn−I, L_{II}, and L_I in acetonitrile (Figure 4a−c) and various other media are similar in the respect that the transient is formed within 10 ns is rather long-lived and has a maximum at $\lambda_a = 470-490$ nm (Table 4). The main decay component has a lifetime (τ_K) ranging from 10 to 120 μs for L_{II} in nonaqueous solvents and from 0.06 to 1 ms for Zn−II (Table 5). The lifetimes for L_I and Zn−I at ambient temperatures are more or less analogous. Exclusion of oxygen has no effect on τ_K, as checked for the four compounds in cyclohexane or acetonitrile. The transient species is attributed to the *trans*-keto tautomer (see Discussion). The presence of the 440 nm peak of Zn−II in nonpolar solvents or the absence of this band, due to exchange of a ligand in polar solvents, does not affect the properties of the observed *trans*-keto tautomer.

Increasing the temperature results in a shorter lifetime for all cases in MCH, acetonitrile or ethanol. The activation energy, obtained from linear Arrhenius plots (Figure 5), is $E_{t-c} = 15$, 14, and 14 kJ mol^{-1} for L_{II} in MCH, acetonitrile, and ethanol, respectively, and about 1 kJ mol^{-1} larger for Zn−II. The main effect is a variation of the preexponential factor, being smallest for Zn−II in acetonitrile, where τ_K is largest. The relative yield of the complexes is larger than for the ligands, and the product $\Phi\epsilon_{480}$ was compared to the reference benzophenone (Table 4). The photocycle is fully reversible because repeated flashing of any of the four compounds did not reveal products in a measurable degree.

The transient was also detected in the IR using the step-scan technique. Photolysis of L_I in dichloromethane shows a bleach-

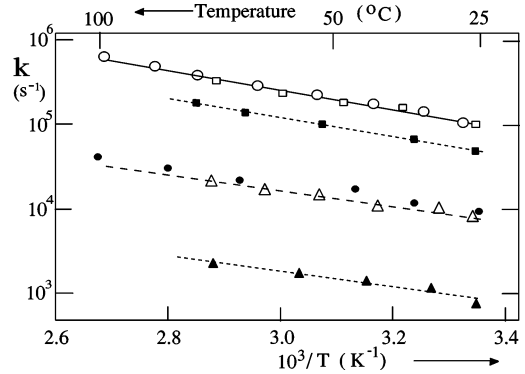


Figure 5. Plots of $1/\tau_K$ vs $1/T$ for L_{II} (open) and Zn−II (full) in MCH (circles), acetonitrile (triangles), and ethanol (squares).

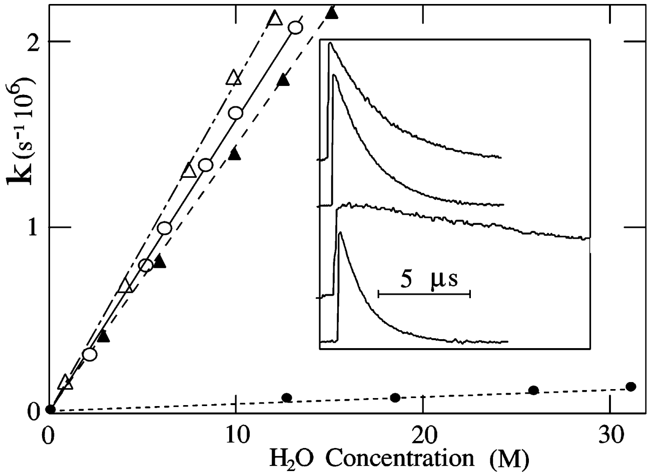


Figure 6. Plots of $1/\tau_K$ vs $[H_2O]$ for L_I (△), L_{II} (○), Zn−I (▲), and Zn−II (●) in ethanol; insets: decay at 460 nm for 2 M water (upper to lower, respectively).

ing at 1627 cm^{-1} and two absorption peaks at 1520 and 1650 cm^{-1} within the 308 nm pulse. The spectrum is similar for L_{II}, and both transients decay with τ_K of ca. 10 μs. The shorter lifetime with respect to $\tau_K = 60-100$ μs (Table 5) is ascribed to a quenching process, taking into account that the substrate concentration, which is required for the IR measurements, is ca. 20 times larger than under UV−vis conditions.

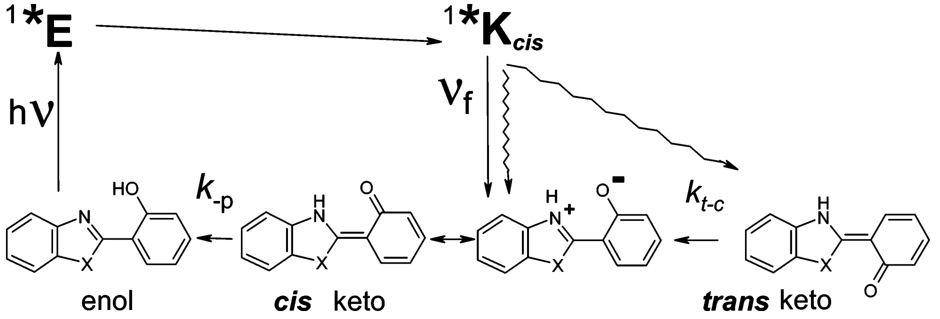
Interestingly, the decay of the transient becomes faster on addition of water. From initially linear plots of $1/\tau_K$ vs $[H_2O]$ in ethanol (Figure 6), rate constants of $k_w = 1.8 \times 10^5$, 1.6×10^5, 1.4×10^5, and 0.2×10^5 M^{-1} s^{-1} were obtained at pH 7 for L_I, L_{II}, Zn−I, and Zn−II, respectively. The transient absorption spectra remain the same as without water. Similar results, in particular the lowest k_w value for Zn−II, were found in mixtures of acetonitrile or *tert*-butyl alcohol with water (Table 4). The decay of the transient of HBO and HBS in acetonitrile was likewise found to become faster on addition of water, the rate constants are $k_w = 1 \times 10^4$ and 2×10^4 M^{-1} s^{-1}, respectively. It is noteworthy that for 2-hydroxybenzenes such a linear dependence has not been reported as yet.

Discussion

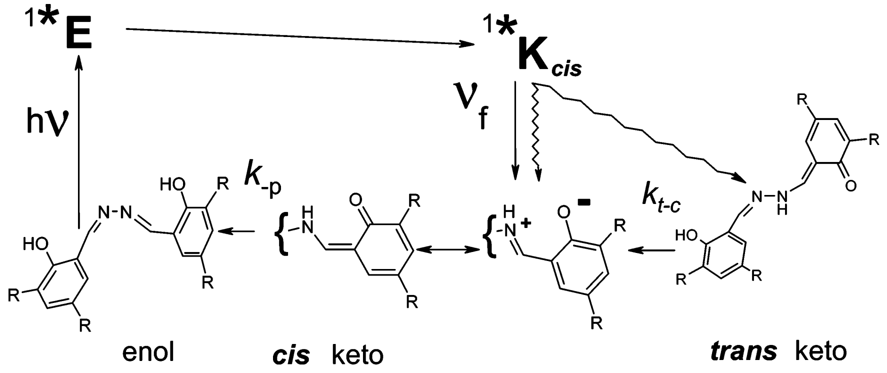
Origin of the Fluorescence. The fluorescence in the 500−600 nm range is suggested to be due to a proton transfer from the hydroxy group to the nitrogen of the methine bond upon excitation of the four compounds examined. Analogous photoprocesses are well-known for HBO or HBS[15−21] and water-soluble 2-hydroxyphenylbenzazoles.[8] A simplified model of the ESIPT mechanism of HBO/HBS via enol → keto tautomerism is illustrated in Scheme 1. The excited singlet enol state (^{1*}E) leads via the fluorescing excited singlet *cis*-keto state ($^{1*}K_{cis}$) to the *trans*-keto form.[21,24,25] The corresponding $^{1*}K_{trans}$ state as source of fluorescence has been excluded.[15−21] Electronic coupling between acidic and basic centers of a 2-hydroxy-*N*-methyl Schiff base and the intramolecular hydrogen bonding and proton-transfer processes play a role. The trans → cis isomerization (rate: k_{t-c}) is rate determining in the thermal relaxation process followed by proton back-transfer (rate: k_{-p}).[16,17,21] Φ_f changes when the amount of water for HBO in dioxane or the hydrogen bonding ability is increased.[27] For 4-benzothiazole and 4-benzazole-type 2-yl-3-hydroxyphenoxyacetic acids[8] in ethanol, the Stokes shift is much smaller than for HBO or HBS in nonpolar solvents.[15,27]

The ESIPT mechanism, now suggested for L_I or L_{II}, is illustrated in Scheme 2. The intramolecular hydrogen bonding and proton transfer processes are probably analogous to HBO/HBS or related 2-hydroxybenzenes. Excitation of the ligand enol form leads to the fluorescing $^{1*}K_{cis}$ state. Fluorescence from the $^{1*}K_{trans}$ state is not compatible with the strong increase in Φ_f on going from fluid to rigid media (Table 3). Internal conversion $^{1*}K_{cis} \rightarrow K_{trans}$ has to be concluded, if also for L_I or L_{II} the rate k_{t-c} for trans → cis isomerization is much smaller than the rate k_{-p} for proton back-transfer. The solvent polarity does not have a large influence on the fluorescence properties. The Stokes shift, here simply based on the excitation and emission maxima (Table 3), of ca. 5000 cm^{-1} for the two Zn complexes is quite large and even larger, 8100−8800 cm^{-1}, in the cases of the ligands. The fluorescence properties are comparable with those of HBO or HBS. A much smaller Stokes shift of ca. 1500 cm^{-1} has been reported for a water-soluble fluorinated HBO in methanol.[7] The values for a Zn complex with a 1,2-benzoquinone diimine ligand in water are $\lambda_f^{em} = 576$ nm, $\tau_f = 1.6$ ns and $\Phi_f = 0.026$.[6] Novel fluorescent Zn sensors, e.g., 3-hydroxy-3-phenyl-1-(*o*-carboxyphenyl)triazene[9] and fluorescein-base[10] Zn^{2+} complexes, were reported in the literature, but their Stokes shifts are small. For a water-soluble fluorinated HBO in methanol, the exchange of the phenolic proton by Zn^{2+} causes a marked enhancement in Φ_f.[7]

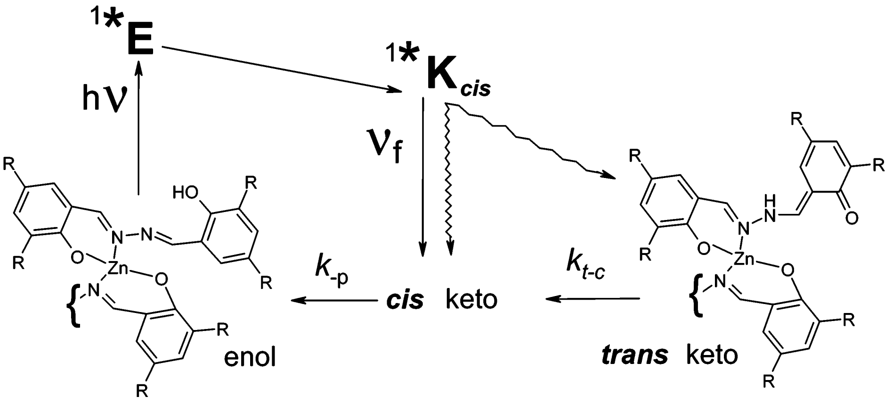
SCHEME 1



SCHEME 2



SCHEME 3



Nature of the Transient of the Ligands. The transient of L_I or L_{II} (parts c and b of Figure 4) could, in principle, be (1) a triplet state, (2) a radical in nature,[33] (3) a solvated electron, (4) a zwitterion, (5) an isomer due to rotation about the C═N double bond or (6) an enol-keto tautomerism. Possibility 1 is excluded because a triplet state reacts with oxygen, but oxygen does not quench the observed transient. Photoionization of phenols and formation of a phenoxyl radical has been reported,[12−14] but possibility 2 of a radical is also unlikely because no reversibility in a first-order reaction would be expected after homolytic cleavage. A second-order decay component was generally present at higher laser intensity, but this could mainly be avoided at a low enough intensity. Radical ions could be formed by photoinduced electron transfer and disappear by electron back-transfer, but the lack of any effect of solvent polarity is not in line with this hypothesis. No solvated electron was observed upon 20 ns 248 nm laser photolysis of the ligands in *tert*-butyl alcohol or methanol, i.e., under conditions where the solvated electron is not scavenged within a few nanoseconds, as is the case in acetonitrile. A minor contribution of solvated electrons could be detected only for Zn−I at higher laser intensity. The absence of photoionization for Zn−II under these conditions indicates slightly different ionization potentials of the two complexes. We therefore conclude that photoejection of an electron (3) does not occur. Possibility 4 is a common photoprocess of heteroaromatics, e.g., spiropyrans,[34] but unlikely for our cases. The isomerization (5) could be hypothesized because of the two C═N double bonds in the ligand. However, the shift in the maximum to $\lambda_a = 480$ nm is too large compared to other cases, e.g., merocyanines, in the literature.[33] We are left with possibility 6 of an enol−keto tautomerism, Scheme 2.

A proton is proposed to be rapidly transferred from the phenolic hydroxy group of L_I and L_{II} to the nitrogen of the methine bond. This involves the *trans*-keto form, which is observed within the pulse width. The back-transfer via the *cis*-keto to the enol form is suggested to be slow trans → cis isomerization and fast proton back-transfer. The lifetime of the *cis*-keto form of 2-hydroxyarenes has been reported to be much shorter than that of the *trans*-keto form.[21−24] For HBO/HBS the values related to the ground state are comparable to L_I and L_{II}, e.g., $\lambda_a = 460$ nm, $\tau_K = 10{-}100$ μs.[17,18,21] However, the reaction mechanism, in particular for HBO, is more complex, owing to intersystem crossing and proton back-transfer via the triplet entity.[15−20] Moreover, a second-order reaction for re-enolization has been observed for HBO in nonpolar solvents.[17,22,24,25] A small amount (a few millimolar) of water is sufficient to open a pathway via proton-catalyzed re-enolization, e.g., for HBO in a nonpolar solvent.[25] On the other hand, the effect of trace water is not significant for HBO in polar media.[26]

ESIPT of the Complexes. The presence of the 440 nm band in the spectrum of the Zn−II complex in nonpolar solvents, the decrease of the absorption at 440 nm in weakly polar solvents such as carbon tetrachloride or dichloromethane, and the absence in more polar solvents indicate an exchange of binding of one ligand. The observed process could be formation of a modified complex due to replacement of one ligand in $Zn_2(LH)_2L$ by water or any solvent of large polarity. However, the presence of the 440 nm peak for Zn−I in nonpolar as well as polar solvents indicates a stable complex $Zn_2(LH)_2L$.

The transient of the complex could be attributed to a metal-centered redox process, but this has to be excluded because Zn^{2+} ions are not redox-active. A phenol-related radical cation and the solvated electron could be expected. However, this photoejection of an electron (3) is not the case for Zn−II as no solvated electron was observed upon 20 ns laser photolysis at 308 nm in *tert*-butyl alcohol or ethanol (see above). The $Zn_2(LH)_2L$ structure shows that intramolecular hydrogen bonding or proton transfer from the phenolic hydroxy group to the nitrogen of the methine bond is possible for the ligands themselves. Only one part of the bis-chromophore of the complex is involved. The ESIPT mechanism for the two Zn complexes is illustrated in Scheme 3.

It is reasonable to conclude that the mechanism of transient formation in all four cases is ESIPT. Intramolecular proton back-transfer is consequently the mechanism of transient decay. The lifetimes in nonaqueous solution, due to trans → cis isomerization followed by proton back-transfer, are comparable but not the same for the ligands and complexes in any given solvent (Table 5). Longer lifetimes for the complexes than the ligands are conceivable because the ligand flexibility in the complex is strongly restricted. The preexponential factor, changing by more than 1 order of magnitude, is sensitive to the solvent, whereas the activation energy, $E_{t-c} = 14-16$ kJ mol^{-1}, is essentially constant (Figure 5).

For the ligands and complexes at −196 °C both viscosity and temperature account for the large increases in Φ_f (Table 3) and τ_f. The viscosity in MCH or ethanol increases by 10−12 orders of magnitude on going from +25 to −196 °C.[35] This has no marked influence on the fluorescence spectra but strongly hinders radiationless deactivation steps competing with fluorescence. The photophysical properties of the four compound in a rigid environment are internal conversion and fluorescence as dominant and minor processes, respectively.

The presence of water accelerates the proton back-transfer (Figure 6), in particular, the enhancing effect of water on the back-transfer is comparable for L_I, L_{II}, and Zn−I (Table 4). Such a proton-catalyzed re-enolation has been observed for HBO,[20] but a linear dependence of $1/\tau_K$ vs [H_2O] has not been reported as yet. For 4-benzothiazole and 4-benzazole-type 2-yl-3-hydroxyphenoxyacetic acids in water, ESIPT is disrupted due to intermolecular hydrogen bonding; metal coordination with Zn^{2+} can also inhibit ESIPT.[8]

The absorption and fluorescence excitation spectra of the complexes reveal the additional 440 nm band with respect to the ligands, probably due to a metal to ligand CT transition. The observed differences due to the ligand vs complex nature concerning ESIPT and back-transfer are relatively small. One could expect a slower back-transfer for the ligand in the complex and this trend was indeed found (Table 5). The function of the *tert*-butyl groups in L_{II} and Zn−II seems to be due to both electronic and steric reasons, but only in small quantity. For example, the fluorescence is virtually not much affected by the bulky groups (Table 2). The longest τ_K value for Zn−II in a variety of solvents indicates a steric effect. On the other hand, a much smaller k_w value for Zn−II in *tert*-butyl alcohol or ethanol (Figure 6) is not due to a shielding. The hydrophobic *tert*-butyl groups may distort a water mediated proton-catalyzed re-enolization reaction in the complex, but the four k_w values are more or less similar in the nonprotic acetonitrile (Table 4).

Conclusion

The fluorescence and transient properties of two ligands and their Zn complexes follow a common pattern that is based on excited-state intramolecular proton transfer from the phenolic hydroxy group to the nitrogen of the methine bond. The excited enol form is converted into the *trans*-keto form with characteristic properties, whereas no phenoxyl radicals are formed. The relaxation via the *cis*-keto form and subsequently by proton back-transfer into the enol form is sensitive to solvent polarity and probably due to structural changes of the 2-hydroxyphenyl moiety with respect to a nearby nitrogen atom. Ligands of the *N,N′*-bis(salicylidene)hydrazine type and the novel complexes are believed to provide a wide application potential.

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Supporting Information Available: X-ray crystallographic files in CIF format for Zn-II, CCDC 279985. This material is available free of charge via Internet at http://pubs.acs.org.

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