Transition Metal Ion Complexes of 2,2′-Bipyridyl-3,3′-diol and 2,2′-Bipyridyl-3-ol: Spectroscopic Properties and Solvent-Dependent Binding Modes

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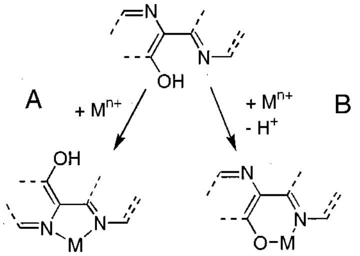
The complexation behaviour of 2,2′-bipyridyl-3,3′-diol and 2,2′-bipyridyl-3-ol, $BP(OH)_2$ and BPOH, with various heavy and transition metal ions has been investigated in aqueous, alcoholic, and acetonitrile solutions. Whereas the complexes with paramagnetic ions and Hg^{II} are non-fluorescent, Zn^{II} and Cd^{II} form highly fluorescent complexes, their coordination geometries depending on the solvent proticity and hydrogen-bond donating ability. Through a comparative study with the corresponding chelates of 2,2′-bipyridyl (bipy), *N,O*-coordination in a six-membered ring chelate has been found to be the dominant binding mode in both the Zn^{II} and Cd^{II} complexes in the protic solvents water and ethanol. Only for Zn^{II} and BPOH is exclusive *N,N′*-chelation found in acetonitrile. NMR measurements on $BP(OH)_2$, BPOH, and bipy in the presence of Zn^{II} and Cd^{II} in acetonitrile confirmed these findings.

Introduction

Controlling the binding modes of metal ion complexes is of particular interest in many fields of bioorganic and bioinorganic chemistry.[1] In many biochemical processes, metal ion complexes with specific or unusual coordination geometries are involved, e.g. in enzymes or metalloproteins.[2] Accordingly, metal ion complexes play an important role in medicinal chemistry and drug design.[3] Here, single conformers of chemically and stoichiometrically identical complexes often show drastically different biological activities.[4] Since many organic ligands possess various heteroatoms and functional groups, competing coordination reactions can interfere. For instance, many aminophilic transition metal ions strongly prefer a five-membered *N,N′*-chelate (route A, Scheme 1) over a six-membered *N,O*-chelate (route B).[5] However, when both binding sites are present in a single molecule as, e.g., in some hydroxy-substituted heterocyclic biaryls or Schiff-base derivatives,[6] the question arises as to how a certain ion coordinates in a particular environment (these features are not only restricted to open-chain ligands but are also found, e.g., in cavity-forming crown compounds).[7] Although important, the chemical nature and structure of the (bi- or multidentate organic) ligand, for instance the geometrical arrangement or flexibility of the molecule, or possible mechanisms of intramolecular stabilization, are not the only decisive factors governing the formation of a specific structure in a certain complex. In liquid media the (counter)ions present and/or the solvent molecules also play a role, depending on the number of free coordination sites at the central ion in the complex (as defined by the geometry of the coordination sphere and the number of chelating ligands present) as well as on the affinity between the metal ion and these other potential (usually monodentate) ligands. Moreover, interactions between the chelating ligand and the solvent can also have an effect on the structural features of a complex, i.e. the proticity or polarity of a particular (solvent) environment can favour certain intra- or intermolecular stabilization modes and can thus either promote or hamper specific central ion−ligand interactions. Especially for chelating ligands that are able to form stabilizing intramolecular hydrogen bonds, e.g. some derivatives of hydroxy-substituted bipyridyls, the proton affinity or protic character of the solvent should play a major role in directing complex formation along, for instance, route A or B (Scheme 1).



Scheme 1. Generalized scheme of possible chelation mechanisms operative in metal ion complexation by hydroxy-substituted *N*-containing heterocyclic biaryls (the structures do not indicate actual complex stoichiometries)

As an extension of our work on the metal ion binding and sensing abilities of 2,2′-bipyridyl-3,3′-diol [$BP(OH)_2$, Scheme 2, A] as well as the spectroscopic properties of its complexes in water,[8−11] we directed our studies towards the characterization of the actual binding modes in these coordination compounds as well as in the corresponding complexes of the reference compound 2,2′-bipyridyl-3-ol (BPOH, Scheme 2, B) in highly polar solvents. Considering the crucial role of the nature of the solvent and counterion, we aimed to elucidate the structures of the complexes dir-

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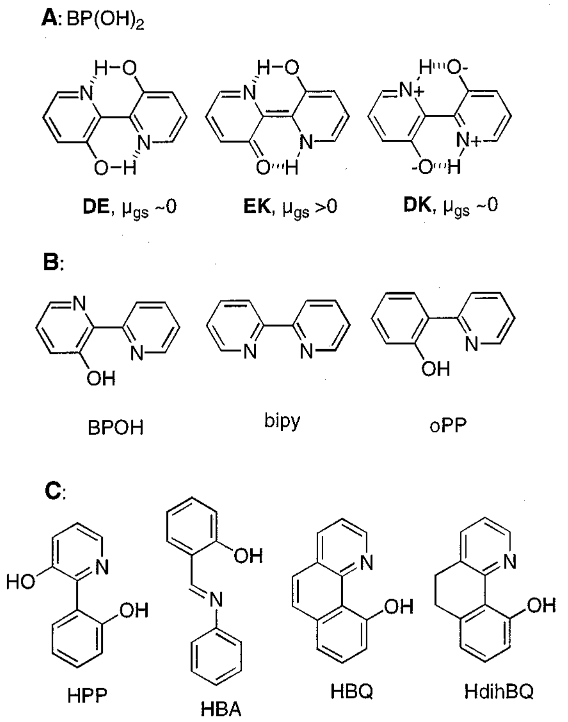
ectly in solution by employing metal ion perchlorates (as weakly donating counterions with a low coordinating ability) and neat, highly polar, protic (water, ethanol) as well as aprotic (acetonitrile) solvents. Moreover, we included the chemically closely related ligand *o*-(2-pyridino)phenol (oPP) and the parent compound 2,2′-bipyridyl (bipy) in our studies (Scheme 2, B). Since in pure water at ambient pH, $BP(OH)_2$ and BPOH only bind to heavy and transition metal ions such as Zn^{II}, Cd^{II}, Cu^{II}, or Ni^{II} and since only the complexes of the first two ions are fluorescent,[8,10,11] the present work focuses on the investigation of the Zn^{II} and Cd^{II} complexes of the (bi)pyridyl ligands by means of absorption, steady-state as well as time-resolved fluorescence, and NMR spectroscopy.



Scheme 2. **A**: Chemical structure and enol-keto tautomerism of $BP(OH)_2$ (DE, EK, DK, and μ_{gs} denote the dienol, enol-keto, and "diketo" tautomers, and the ground state dipole moment, respectively); **B**: chemical structures of the investigated BPOH, bipy, and oPP; **C**: chemical structures of related HPP, HBA, HBQ, and HdihBQ

Results and Discussion

Uncomplexed Ligands

The photophysical properties of uncomplexed $BP(OH)_2$ and BPOH in water, ethanol, and acetonitrile are included in Table 1.

In accordance with results published by other research groups,[12−16] $BP(OH)_2$, with its two strong internal hydrogen bonds (Scheme 2, A), shows the characteristic features of ESIPT (*e*xcited *s*tate *i*ntramolecular *p*roton *t*ransfer) fluorescence in polar organic solvents. Thus, the absorption and emission bands are broad, structureless, and largely Stokes-shifted (absorption and fluorescence excitation spectra match) and are centred at the same energies as in apolar or medium polarity organic solvents (Table 1). Consequently, the photophysical mechanism involves excitation of the only stable ground-state dienol (DE) tautomer, an ultrafast double ESIPT process,[17] and emission from a zwitterionic "diketo" ($^1DK^*$) tautomer. Besides unchanged spectral features, with increasing solvent polarity and proticity radiationless deactivation of the excited singlet state(s) is enhanced, resulting in larger rate constants for non-radiative decay on going from *n*-hexane [$k_{nr} = (1 - \varphi_f)/\tau_f = 2.2{\cdot}10^8\ s^{-1}$] to acetonitrile ($9.0{\cdot}10^8\ s^{-1}$). As possible mechanisms accounting for the non-radiative loss of energy of $^1DK^*$, solute−solvent interactions (especially in protic solvents), torsional motions of the two pyridyl rings or the occurrence of *t*wisted *i*ntramolecular *c*harge *t*ransfer (TICT), the proximity effect (due to close-lying $n\pi^*$ states), and triplet population are discussed.[13,16,18,19]

In water, the intramolecular hydrogen bonds are partially broken up and stabilization of the planar conformation is reduced resulting in a spectroscopically very different ground-state behaviour and reduced fluorescence quantum yields.[8,10,11,15,20] For the doubly-distilled water employed here (pH = 6.4, see Experimental Section), the positions of the global and second absorption band maxima are included in Table 1. In contrast, the fluorescence spectrum consists of the characteristic strongly Stokes-shifted band suggesting that upon excitation all the various conformers or tautomers undergo rapid transformation to emissive $^1DK^*$. Accordingly, k_{nr} ($= 21.3{\cdot}10^8\ s^{-1}$) is also increased in water. In pure doubly-distilled water, time-resolved fluorescence measurements revealed bi-exponential decays with a relative amplitude of ≥ 0.98 for the main emitting species (Table 1), but since this behaviour is not critical with regard to the results and interpretations of the present complexation experiments, we will not go into further detail here (the same holds true for BPOH, see below.).

In the case of BPOH, the position of the absorption band in aprotic solvents is also independent of the solvent polarity. The emission band of very weak intensity is largely Stokes-shifted and, due to a non-zero dipole moment of the emitting monoketo tautomer, its spectral position is more strongly solvent polarity-dependent than that of $^1DK^*$ of $BP(OH)_2$ {$\Delta\tilde{\nu}$(abs−em) [MeCN−3-MP] = 1000 cm^{-1} for BPOH cf. $\Delta\tilde{\nu}$(abs−em) [MeCN−Hex] = 300 cm^{-1} for $BP(OH)_2$; Table 1}.[13,16,21,22] The weaker fluorescence of BPOH as compared to $BP(OH)_2$ is mainly due to enhanced flexibility (with possible TICT-state formation), based on the lack of a second stabilizing hydrogen bond, and low-lying $n\pi^*$ transitions.[13,16]

In protic solvents, solute−solvent interactions change the fluorescence behaviour of BPOH, i.e. the emission spectrum is blue-shifted and the fluorescence quantum yield increases (ethanol cf. acetonitrile in Table 1), but in alcohols the absorption spectrum remains unchanged. Only water induces stronger effects and a red-shifted shoulder appears in the absorption spectrum while emission occurs at 23000 cm^{-1}. Although the fluorescence quantum yield increases further on going from ethanol to water, it is still much lower than that of $BP(OH)_2$ and thus hampered fluorescence lifetime

Table 1. Spectroscopic data for $BP(OH)_2$ and BPOH in various solvents at 298 K

	Solvent[a]	ε_r[b]	$\tilde{\nu}$(abs) [10^3 cm^{-1}]	$\tilde{\nu}$(em) [10^3 cm^{-1}]	$\Delta\tilde{\nu}$(abs−em) [cm^{-1}]	φ_f	τ_f [ns]
$BP(OH)_2$	Hex	1.9	29.2	19.8	9400	0.30	3.1
	Et_2O	4.3	29.4	19.6	9800	0.21	2.6
	MeCN	35.9	29.4	19.7	9700	0.09	1.0
	EtOH	24.6	29.4	20.7	8700	0.18	2.1
	MeOH	32.7	29.2	20.8	8400	0.10	1.2
	H_2O	80.2	28.8,[c] 24.8 (23.2)	21.3 (23.6)	7500	0.04[d]	0.45, 4.8[e]
BPOH	3-MP	1.9	30.8[f]	17.8[f]	13000[f]	$5.5\cdot10^{-3}$[g]	[h]
	Et_2O	4.3	30.8[i]	17.1[i]	13700[i]	n.r.[j]	n.r.
	MeCN	35.9	30.9	16.9	14000	$1.3\cdot10^{-4}$	n.d.[k]
	EtOH	24.6	30.9	17.2	13700	$1.2\cdot10^{-3}$	n.d.
	H_2O	80.2	31.3[l] (27.0)	23.0	8300	$5.0\cdot10^{-3}$ [d]	n.d.

[a] Hex = *n*-hexane, Et_2O = diethyl ether, MeCN = acetonitrile, EtOH = ethanol, MeOH = methanol, 3-MP = 3-methylpentane. – [b] Ref.[65]. – [c] Global maximum (see Figure 1, B), ratio of 28.8:24.8:23.2 = 2.4:1.4:1. – [d] With excitation at the absorption maximum. – [e] Relative amplitudes vary with excitation and emission wavelength and are always > 0.98 for the fast component. – [f] Ref.[22]. – [g] Ref.[24]. – [h] The room temperature fluorescence lifetime data published to date are controversial: whereas Tokumura et al. reported bi-exponential decay kinetics with lifetimes of 80 and 410 ps,[22] Kaczmarek et al. reported a value of 3.02 ns.[24] – [i] Ref.[16]. – [j] Not reported. – [k] Not determined due to limited time resolution of the instrumental set-up employed. – [l] Global maximum, ratio of 31.3:27.0 = 7.9:1.

measurements with the instrumental set-up employed (temporal resolution >100 ps).

The importance of the two internal hydrogen bonds in $BP(OH)_2$ is additionally stressed by the fact that similar observations as for BPOH were made for all the "flexible" related compounds, oPP (investigated here and in refs.[23,24]), HPP,[24] and HBA[25] (Scheme 2, C) in organic solvents, in which they are at best only weakly fluorescent (in aqueous solutions of $0.5 < pH < 13.5$, oPP is non-fluorescent[26,27]). On the other hand, all those compounds that are effectively "forced" to be planar are at least moderately fluorescent, e.g. HBQ[23,28,29] and HdihBQ[23] (Scheme 2, C), supporting the generally accepted reaction scheme outlined above. Most probably, besides close-lying $n\pi^*$ states, rapid torsional motions break up the tight intramolecular hydrogen bond detected for some of these compounds in the ground state through the appearance of a characteristic signal at low field in the ^1H NMR spectra, i.e. at $\delta = 14.14$ for BPOH, at $\delta = 14.51$ for $BP(OH)_2$ (see below), and at $\delta = 14.3$ for oPP.[30]

The parent compound bipy is very weakly or non-fluorescent in pure water at room temperature. However, the origin of the weak fluorescence reported in some publications is still a matter of debate.[31]

Complexes

Before going into detail on the different binding modes of the fluorescent complexes of $BP(OH)_2$ and BPOH, the general implications concerning the effects of para- and diamagnetic cations, ion selectivities, complex stoichiometries, as well as the main absorption and emission features will be discussed, as exemplified by the complexes of $BP(OH)_2$ in water.

Complexes of $BP(OH)_2$ in Water

Steady-State Absorption and Fluorescence

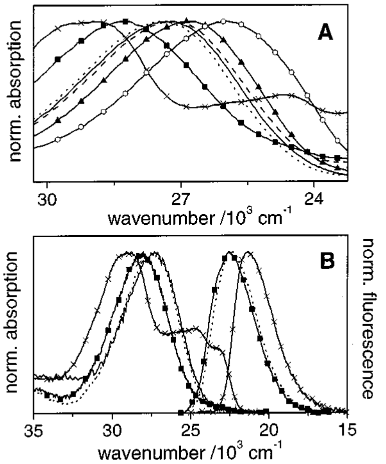


Figure 1. Normalized steady-state absorption spectra of [$M^{II}\subset BP(OH)_2$] in pure water: **A**: free $BP(OH)_2$ (×) and complexes with Cd^{II} (■), Zn^{II} (· · · ·), Hg^{II} (–), Co^{II} (– – –), Ni^{II} (▲), and Cu^{II} (○); **B**: Spectra of the d^{10} metal ion complexes [excitation at 370 nm, $Hg^{II}\subset BP(OH)_2$ is non-fluorescent]; for both plots, c_L = $3\cdot10^{-6}$ M and c_M = $5\cdot10^{-5}$ (Cu^{II}), $1\cdot10^{-4}$ (Ni^{II}), $1\cdot10^{-3}$ (Co^{II}, Hg^{II}), $3\cdot10^{-3}$ (Zn^{II}), $7\cdot10^{-3}$ (Cd^{II}), i.e. full complexation is achieved

In pure water, only complexation to the metal ions Zn^{II}, Cd^{II}, Hg^{II}, Cu^{II}, Ni^{II}, and Co^{II} leads to a change in both the absorption (Figure 1, A) and emission spectra (shown for the d^{10} metal ions in Figure 1, B); no effects are observed for Fe^{II}, Mn^{II}, or Pb^{II}, nor for Ca^{II}, Mg^{II}, or Na^{I}. Whereas the complexes $BP(OH)_2$ forms with paramagnetic transition metal ions, i.e. Cu^{II} or Ni^{II}, are non-fluorescent, in the case of the diamagnetic heavy metal ions of the d^{10} group, only Hg^{II} forms a non-fluorescent complex (Figure 1, B). The Zn^{II} and Cd^{II} complexes are highly fluorescent (Figure 1, B).[8,10,11] The spectroscopic data are collected in Table 2; the full overlap of the absorption bands of the complexes and the free ligand follows from Figure 1.

For all the complexes, the absorption bands of lowest energy remain ligand-centred electronic transitions of $\pi\pi^*$ nature showing typical features of absorption bands of organic chromophores, i.e. broad, structureless bands with relatively high extinction coefficients ($\varepsilon > 10^3$ $M^{-1}\cdot cm^{-1}$). Metal-centred d-d transitions were not observed at the concentrations used and, in the case of the paramagnetic ions,

Table 2. Spectroscopic properties and apparent complex stability constants (see text) of the complexes of $BP(OH)_2$ in water at 298 K

M^{II}	$\tilde{\nu}$(abs) [10^3 cm^{-1}]	$\tilde{\nu}$(em) [10^3 cm^{-1}]	φ_f	τ_f [ns]	log K^{app}
Cu^{II}	26.0	–	–	–	5.9
Ni^{II}	26.9	–	–	–	5.0
Co^{II}	27.1	–	–	–	4.7
Zn^{II}	27.5	22.5	0.62	6.17	4.2
Cd^{II}	28.2	22.6	0.53	5.24	3.6
Hg^{II}	27.3	–	–	–	4.4

no metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge-transfer bands were found. However, due to its exceptional features (internal hydrogen bonds, enol-keto tautomerism), the characteristic shifts often observed upon complexation are obscured by the very broad absorption spectrum of $BP(OH)_2$ in neat aqueous solution. For example, with 8-hydroxyquinoline (8-HQ), the absorption bands of the metal ion complexes are well-separated and red-shifted by ca. 4500 cm^{-1}, most probably due to a more covalent nature of the transition metal−quinoline nitrogen bond.[32] Similar shifts as for 8-HQ are observed for the complexes of bipy (4460 cm^{-1} for the Zn^{II} complex, see below), but in the case of $BP(OH)_2$ the bands are strongly overlapped and only the maximum of the main band is slightly red-shifted (Figure 1).

Opposite tendencies can be derived from the emission measurements, i.e. different effects of para- and diamagnetic cations with strong similarities within each group, the only exception being Hg^{II}. All the paramagnetic ions and Hg^{II} quench the fluorescence without any spectral shifts, suggesting static quenching to be the main force. The emission spectra of the Zn^{II} and Cd^{II} complexes are very similar and largely overlap with the emission band of the free ligand [blue-shifted by ca. 20 nm (≈1000 cm^{-1}), Figure 1, B].[10,11] Fluorescence excitation spectra recorded at full complexation resemble the absorption spectra of both the Zn^{II} and Cd^{II} cation complexes.

Spectroscopic Titrations and Complex Stoichiometry

For all the cations studied, isosbestic points are observed in their UV/vis spectrophotometric titrations [as an example, see the titration of $BP(OH)_2$ with Cu^{II} in ref.[9]; for fluorometric titrations and the opposite effects of para- and diamagnetic cations, see Figure S2, Supplementary Material]. Analysis of the titration data according to the method of continuous variations[33] yielded a complex stoichiometry of 1:2, i.e. ML_2 (see ref.[9]; an example of an analysis according to this method is given in the Supporting Information). In all the UV/vis spectrophotometric and fluorometric titrations performed with $BP(OH)_2$ and various metal ions, no divergent spectral features were found, making a discrimination between the 1:1 and 1:2 complexes impossible in this way. However, fitting the titration curves was only found to yield acceptable results for a sum of a 1:1 and a 2:1 complexation model[34] in some cases (Zn^{II}, Cd^{II}), both complexes showing similar spectroscopic behaviour. For the other, more strongly coordinating ions, the complex stability constants are too high to be reliably determined by this method and the relatively poor solubility of $BP(OH)_2$ in terms of a c_{L0} titration (see Experimental Section) made such a reverse titration (titration of M with L) impossible. Thus, in order to compare the binding strengths of all the cations, the apparent complex stability constants log K^{app} were determined spectroscopically and are included in Table 2 (for a description of the procedure, see Experimental Section). As can be deduced from Table 2, the order of log K^{app} can be described by the Irving−Williams order[35] and the ion selectivity is comparable to that shown by other so-called "general" ligands with bidentate *N*,*O*-chelating sites such as 8-HQ, pyridine-2-carboxylic acid, or aryl-azomethine ligands.[6,36−39] Provided they are not significantly conformationally restricted, these ligands do not show any enhanced selectivity for particular ions.[6,36]

On analysis of the fluorescence excitation spectra recorded for solutions containing different amounts of free ligand and complex, the spectra could always be described by a linear combination of the fluorescence excitation spectra of the free ligand and the 1:1 complex. Thus, the 1:1 and 1:2 complexes show identical fluorometric behaviour and cannot be distinguished by steady-state fluorescence spectroscopy either.

Time-Resolved Fluorescence

The effect of complexation on the fluorescence decay kinetics of $BP(OH)_2$ reflects the observations made by means of the steady-state fluorescence experiments. Addition of quenching ions such as Cu^{II} and Hg^{II} to a solution of $BP(OH)_2$ in water leads only to a slight variation in fluorescence lifetime but to a strong decrease in the amplitude, when comparing the photons emitted over a certain time interval, i.e. static quenching occurs (this is observed at any combination of excitation and emission wavelengths).

In contrast, for Zn^{II} and Cd^{II}, in agreement with an increase in fluorescence quantum yield, a chelation-induced increase in fluorescence lifetime is observed, leading to the appearance of a new long-lived fluorescence decay component, its lifetime being cation specific (Table 2).[8,10,11] A time-resolved fluorometric titration reveals that with increasing metal ion concentration the relative amplitude of the short-lived decay component decreases and, correspondingly, the relative amplitude of the long-lived decay component increases. No ion concentration-dependent variations in the lifetime of the long-lived decay component are evident, thus supporting the observations made by steady-state spectroscopy, i.e. identical spectroscopic behaviour of the 1:1 and 1:2 complexes. This is also confirmed by fluorescence decay measurements at different emission wavelengths and global analysis of the data. Thus, ground-state heterogeneity[11] can be assumed and suggests that fluorescence deactivation is fast as compared to excited-state decomplexation, i.e. the complexes are stable in both the ground and excited states.

The faster decay of the fluorescence of the Cd^{II} complex can be rationalized in terms of the heavy atom effect.[40] Assuming that in the tightly bound complexes the main route of non-radiative deactivation is intersystem crossing ($k_{nr} \approx k_{isc}$), the heavy atom effect can be quantified by using a central field single-electron approximation for the relationship between k_{isc} and the spin−orbit coupling constant.[41] Accordingly, $\log k_{nr} + \log n^6$ (n = quantum number) gives a measure of the heavy atom effect and the values calculated for the Zn^{II} and Cd^{II} complex amount to 11.4 and 12.1, in good agreement with published values for the related 8-HQ complexes of these ions.[41]

Binding Modes of the Zn^{II} and Cd^{II} Complexes of the (Substituted) Bipyridyls (and oPP) in Water, Ethanol, and Acetonitrile

Although the spectroscopic behaviour of the complexes of BP(OH)$_2$ reveals certain tendencies, the real nature of the complexes in terms of Scheme 1 and the background given in the Introduction is still unclear. A theoretically possible route C (not shown in Scheme 1), the formation of a sterically unfavoured seven-membered ring due to coordination to both hydroxyl groups, can be ruled out on the basis of thermodynamic considerations.[42,43] The necessary deprotonation of two hydroxyl groups at pH ≈ 7, the order of complex stability constants (the highest K is observed for the aminophilic cation Cu^{II}), the general preferences of the "soft" metal ions (in terms of Pearson's concept of hard and soft acids and bases)[44] for "soft" donor heteroatoms, and the unfavoured geometry of the resulting chelate render this mechanism very unlikely. However, chelate formation according to routes A and B in Scheme 1 has to be considered, as has been shown by Cargill Thompson et al.[45]

Before going into detail on the various complexes, it is noteworthy that whereas BP(OH)$_2$, BPOH, and bipy show complexation-induced spectroscopic effects upon addition of Zn^{II} and Cd^{II} in all three solvents investigated, very weakly fluorescent oPP ($\varphi_f < 10^{-5}$) does not show any pronounced changes in its photophysical properties upon addition of cations. Even in organic solvents, only small effects are observed at a high excess of metal ion (e.g. >500-fold excess of Zn^{II}). Thus, the behaviour of oPP will be discussed separately below. The spectroscopic data for the Zn^{II} and Cd^{II} complexes of BPOH and bipy are reported in Table 3, along with the data for the corresponding BP(OH)$_2$ complexes.

Absorption and Fluorescence Spectroscopy in Water

In pure water, the Zn^{II} and Cd^{II} complexes of both BPOH and BP(OH)$_2$ show very similar absorption and emission behaviour (Figure 2, Table 3). The spectral band

Table 3. Spectroscopic properties of the Zn^{II} and Cd^{II} complexes of BP(OH)$_2$, BPOH, and bipy in water (W), ethanol (E), and acetonitrile (A; So. = solvent)

Ion /So.	Ligand	$\tilde{\upsilon}$ (abs) [10^3 cm^{-1}]	$\tilde{\upsilon}$(em) [10^3 cm^{-1}]	$\Delta\tilde{\upsilon}$(abs–em) [cm^{-1}]	ϕ_f	τ_f [ns]	k_f [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
Zn^{II} / W	BP(OH)$_2$	27.5	22.5	5000	0.62	6.17	1.00	0.61
	BPOH	27.0	21.8	5200	0.59	6.71	0.88	0.61
	bipy	33.9	30.8	3100	0.34	1.43	2.38	4.61
Zn^{II} / E	BP(OH)$_2$	25.6	21.5	4100	0.55	6.07	0.91	0.74
	BPOH[a]	25.2	20.8	4400	(0.26)		-	-
	BPOH[b]	30.0[c]	20.6 (26.6)[d]	9400	0.47	6.21	0.76	0.85
	bipy	33.9	30.8	3100	0.10	0.72	1.39	12.5
Zn^{II} / A	BP(OH)$_2$[a]	24.7	21.8	2900	-	6.01	-	-
	BP(OH)$_2$[e]	30.5[f]	25.5, 20.6	5000, 9900	n.d.[g]	1.37[h]	-	-
	BP(OH)$_2$[e]	24.7	21.8	2900	0.47	5.87	(0.80)	(0.90)
	BPOH	30.4[c]	27.5	2900	0.36	1.31	2.75	4.88
	bipy	33.9	30.6	3300	0.27	1.48	1.82	4.93
Cd^{II} / W	BP(OH)$_2$	28.2	22.6	5600	0.53	5.24	1.01	0.90
	BPOH	27.2	22.0	5200	0.48	5,79	0.92	0.99
	bipy	33.9	30.8	3100	0.05	0.29	1.72	32.7
Cd^{II} / E	BP(OH)$_2$	26.7	22.0	4700	0.54	5.30	1.02	0.87
	BPOH[a]	26.0	21.0	5000	(0.26)		-	-
	BPOH[b]	30.2[c]	21.1	9100	0.45	5.50	0.82	1.00
	bipy	33.9	30.8	3100	0.05	0.29	1.92	30.5
Cd^{II} / A	BP(OH)$_2$	27.6	22.2	5400	0.46	5.18	0.89	1.04
	BPOH	30.7[c]	27.4 (21.1)	3300	0.10[i]	0.26[j]	3.85	34.6
	bipy	33.9	30.8	3100	0.07	0.23	3.04	40.4

[a] Intermediate complex observed in the titration experiments at $x_{M/L} \leq 0.5$. − [b] Data obtained at highest ion excess (ML complex). − [c] Center of the band displaying a double maximum. − [d] Intensity of the band at 26600 cm^{-1} ca. one-hundredth of the total fluorescence intensity. − [e] Data obtained at highest Zn^{II} excess possible: two different absorption and emission bands. − [f] From fluorescence excitation spectrum. − [g] Not determined because full complexation could not be reached. − [h] Observed at 25500 cm^{-1}; τ_1 = 0.61 ns and τ_2 = 5.30 ns when recorded at 21800 cm^{-1}. − [i] φ_f^{rel} (band at 21100 cm^{-1}) = 0.02. − [j] τ_2 = 5.44 ns (a_{rel} = 0.27) when observed at 21100 cm^{-1}.

positions for both absorption and emission differ by ≤ 1000 cm^{-1} and the fluorescence quantum yields and lifetimes are very similar as well. Consequently, this leads to similar rate constants for radiative and non-radiative deactivation.

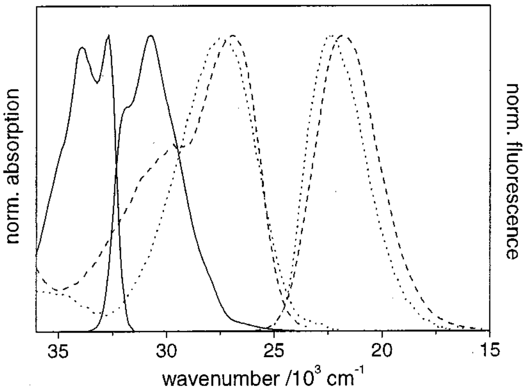


Figure 2. Steady-state spectra of the Zn^{II} complexes of $BP(OH)_2$ (· · · ·), BPOH (— — —), and bipy (—) in pure water [full complexation; excitation at absorption maximum; $c_L = 3 \cdot 10^{-6}$ M, $c_M = 7.5 \cdot 10^{-5}$ M in the case of bipy, $1 \cdot 10^{-3}$ in the case of BPOH, and for $BP(OH)_2$ see caption of Figure 1]

On the other hand, the behaviour of the corresponding complexes of bipy is clearly different. The Stokes shifts observed are only two-thirds the size of those observed for the hydroxy bipyridyls, the fluorescence quantum yields are considerably lower, and, in particular, the fluorescence decays more rapidly by a factor of ca. 4.5.

Accordingly, this effect should be predominantly reflected in different k_{nr} values. Indeed, the value found for $Zn^{II}{\subset}$bipy, for example, is almost an order of magnitude greater than those obtained for $Zn^{II}{\subset}$BPOH and $Zn^{II}{\subset}BP(OH)_2$. This effect is even more pronounced in the case of Cd^{II}. Thus, the "activity" of $n\pi^*$ state interaction is higher in the bipy complexes than in the other two complexes and the influence of the heavy atom (or ion) Cd^{II} is more pronounced in the case of these smaller chelates with a five-membered ring structure [note that because of the higher stability of the bipy complexes (see below), enhanced torsional motions about the central bipyridyl bond seem to play only a minor role]. Furthermore, besides the shift in absorption (electrostatic polarization induced by M^{II}), $M^{II}{\subset}$bipy complexes show the characteristically structured absorption bands, with the vibrational structure being better resolved.[46] On the other hand, on comparing k_f and k_{nr} of $M^{II}{\subset}BP(OH)_2$ with those of free $BP(OH)_2$, it is obvious that the rate constant for fluorescence deactivation remains constant (within experimental error, Table 1), but that the contributions of competing non-radiative deactivation channels of the first excited singlet state are markedly reduced [it is interesting to note that tight binding of $BP(OH)_2$ in the complexes further reduces k_{nr} by a factor of 3.5 as compared to k_{nr} in apolar solvents such as *n*-hexane ($k_{nr} = 2.2 \cdot 10^8 s^{-1}$)].

Absorption and Fluorescence Spectroscopy in Ethanol

Ethanol, being less polar than water but still capable of hydrogen-bond formation, induces similar effects as water, but some noticeable differences in complex formation are observed, especially in the case of BPOH. For $M^{II}{\subset}BP(OH)_2$ and $M^{II}{\subset}$bipy, a behaviour similar to that in water is observed. The only deviations are slightly blue-shifted spectra in the case of $M^{II}{\subset}BP(OH)_2$ and a marked drop in fluorescence quantum yield and lifetime for the Zn^{II} complex of bipy. The exceptional behaviour of this complex in ethanol is unclear and will not be discussed further. However, the data obtained for $Zn^{II}{\subset}$bipy are still different from those measured for the corresponding complexes of its hydroxy derivatives. $Cd^{II}{\subset}$bipy shows the expected features and, in acetonitrile (see below), the behaviour of $Zn^{II}{\subset}$bipy is again comparable to that in water.

For M^{II}/BPOH, complex formation is very remarkable. At low metal ion concentrations up to a metal-to-ligand ratio $x_{M/L} = 0.5$, the complex formed resembles that of $BP(OH)_2$. In Figure 3, A, the UV/vis spectrophotometric titration spectra for BPOH with Zn^{II} up to $x_{M/L} = 0.5$ are displayed, clearly showing the characteristic features (see Table 3 for the corresponding data). On addition of more Zn^{II} to the solution, the band at 25200 cm^{-1} diminishes and a new band appears at 30000 cm^{-1} (Figure 3, B). This band displays the typical characteristics of the $Zn^{II}{\subset}$bipy complex (blue-shifted and structured, cf. A and B, Figure 4). However, the emission spectra measured up to a 1000-fold excess of Zn^{II} (e.g. "— — —" in Figure 4, A) resemble that of $Zn^{II}{\subset}BP(OH)_2$ (Figure 4, B, " · · · · ") and the fluorescence decay has almost the same lifetime (Table 3).

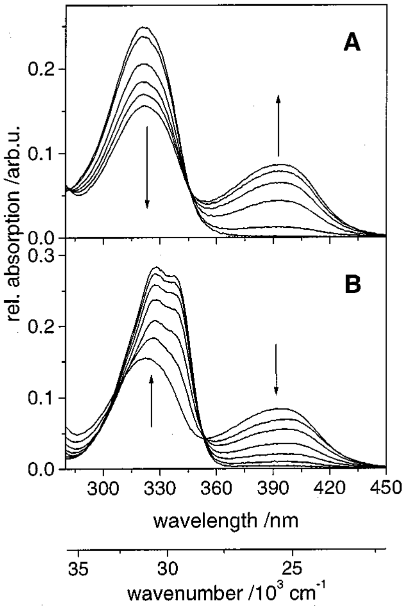


Figure 3. UV/vis spectrophotometric titration of BPOH with Zn^{II} in ethanol; **A**: steps for $x_{M/L} = 0.1-0.5$; **B**: steps for $x_{M/L} = 0.5-50$ (arrows indicate changes upon Zn^{II} addition); measurements were performed in 100 mm absorption cells with $c_L = 3.7 \cdot 10^{-6}$ M; the second *x* axis (wavenumber scale) is included for better comparison with data presented in the text and tables

Only on the high energy side (enlarged emission spectrum marked "—" in Figure 4, A) is a weak band centred at 26600 cm^{-1} visible. In view of the emission properties of $Zn^{II}{\subset}$bipy, i.e. low φ_f and fast decay kinetics, emission from

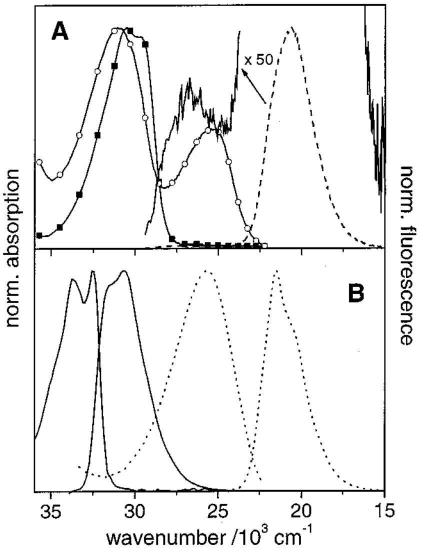


Figure 4. Steady-state spectra of the Zn^{II} complexes of the (substituted) bipyridyls in ethanol; **A**: absorption spectra of Zn^{II}⊂(BPOH)$_2$ (○), Zn^{II}⊂BPOH (■), and emission spectrum of Zn^{II}⊂BPOH (– – – –); the enlarged high-energy side (–) of the emission spectrum is also included ($c_L = 3 \cdot 10^{-6}$ M, $c_M = 1.5 \cdot 10^{-3}$ M); **B**: spectra of the Zn^{II} complexes of BP(OH)$_2$ (· · · ·) and bipy (–) in ethanol (full complexation; excitation at absorption maximum; $c_L = 3 \cdot 10^{-6}$ M, $c_M = 7.5 \cdot 10^{-5}$ M)

an *N*,*N*′-chelated Zn^{II}⊂BPOH complex might be expected to be weak in ethanol as well. However, the fluorescence excitation spectra recorded at 27000 cm^{-1} and 20800 cm^{-1} are similar and resemble the absorption spectrum of the 1:1 complex centred at 30000 cm^{-1}. Furthermore, closer inspection of Figure 4 provides a possible explanation for the fluorometric results. Assuming that in an equilibrium situation involving intermediately formed "Zn^{II}⊂BP(OH)$_2$-like" complexes still in the solution, light emitted from the "Zn^{II}⊂bipy-like" complex is absorbed by this species and is then re-emitted with its characteristic stronger fluorescence, the blue-shifted emission of the "Zn^{II}⊂bipy-like" complex should be quenched.

Absorption and Fluorescence Spectroscopy in Acetonitrile

In acetonitrile, a solvent of comparable polarity lacking H-bond donating ability, the tendencies observed in ethanol are even more pronounced. Only the Cd^{II} complex of BP(OH)$_2$ shows almost identical spectroscopic features in all three solvents employed. For Zn^{II}/BP(OH)$_2$, the metal ion concentration-dependent spectroscopic behaviour resembles that of Zn^{II}/BPOH in ethanol. At low concentrations, the features seen for Zn^{II}⊂BP(OH)$_2$ in aqueous solution are observed, but with a large excess of Zn^{II}, a blue-shifted band centred at 25500 cm^{-1} appears in the emission spectrum (Figure 5). The changes in absorption are negligible but in Figure 5 the differences between the fluorescence excitation spectra recorded in both emission bands can be seen. Observation at 19200 cm^{-1} yields a band corresponding to the absorption band of the 1:2 complex (cf. the close similarity of the spectra marked "–" and " ○" in Figure 5). Furthermore, emission wavelength-dependent fluorescence decay data support the results (1.37 ns at 25500 cm^{-1} cf. ca. 6 ns at 21800 cm^{-1}, see Table 3).

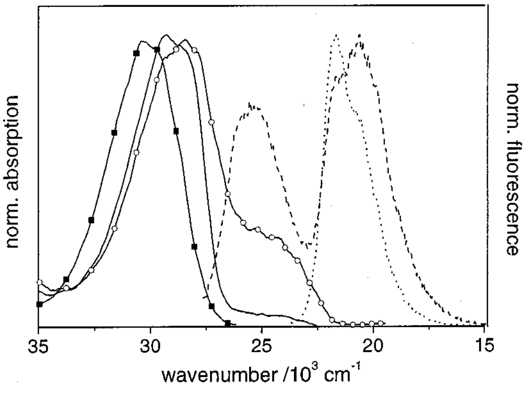


Figure 5. Steady-state spectra of Zn^{II}/BP(OH)$_2$ in acetonitrile; absorption (–) and emission (· · · ·, excitation at 24500 cm^{-1}) spectra of the ML$_2$ complex; emission spectrum at high Zn^{II} excess (both complexes present, – – –, excitation at 29500 cm^{-1}), and fluorescence excitation spectra at high Zn^{II} excess (observation at 25600 cm^{-1} = ■; observation at 19200 cm^{-1} = ○)

For Zn^{II}⊂BPOH, only the absorption band at 30400 cm^{-1} and an emission band at 27500 cm^{-1} are seen, irrespective of the Zn^{II} concentration (Table 3). The similarity between the photophysical properties of Zn^{II}⊂bipy and Zn^{II}⊂BPOH, including typical characteristics (vibrational structure) of the M^{II}⊂bipy absorption bands, is remarkable (Table 3 and Figure S3, Supplementary Material). The higher-energy emission band, absent in ethanol, indicates the formation of a "Zn^{II}⊂bipy-like" chelate in acetonitrile. In accordance with the different behaviour of the Zn^{II} and Cd^{II} complexes of BP(OH)$_2$, for Cd^{II}/BPOH some "Cd^{II}⊂BP(OH)$_2$-like" chelate is still observed at low Cd^{II} concentrations.

The data presented thus far lead to the conclusion that the complexes investigated can be divided into two groups according to their spectroscopic behaviour in the different solvents [these "spectroscopic reference structures" are termed "Zn^{II}⊂bipy-like" and "Cd^{II}⊂BP(OH)$_2$-like"].

Zn^{II}/BP(OH)$_2$: "Cd^{II}⊂BP(OH)$_2$-like" in all the solvents except in acetonitrile at high excess of Zn^{II};

Zn^{II}/BPOH: "Cd^{II}⊂BP(OH)$_2$-like" in water and at low metal ion concentrations in ethanol, "Zn^{II}⊂bipy-like" in acetonitrile and at high metal ion concentrations in ethanol;

Cd^{II}/BPOH: "Cd^{II}⊂BP(OH)$_2$-like" in water and at low metal ion concentrations in ethanol and acetonitrile, "Zn^{II}⊂bipy-like" at high metal ion concentrations in ethanol and acetonitrile;

Cd^{II}/bipy: "Zn^{II}⊂bipy-like".

The fact that the bipy complexes display their characteristic behaviour in all the solvents and that the only other chelate structure that may conceivably be formed in the complexes of the hydroxy derivatives is that arising from *N*,*O*-chelation indicates that this structure is most probably the favourable one for the chelates of the *o*-hydroxy bipyridyls in protic solvents. Unfortunately, due to the different behaviour of oPP (see below), *N*,*O*-chelates could not be directly detected by means of optical spectroscopy and thus ^{1}H NMR experiments were additionally performed. [Note that complexation of $BP(OH)_2$ to Cu^{II} in acetonitrile does not lead to the formation of an *N*,*N'*-chelate. The main absorption band remains centred at ca. 29000 cm^{-1}, but the shape of the spectrum very much resembles that of $BP(OH)_2$ in pure water, i.e. the Cu^{II} complex displays a second maximum at 23800 cm^{-1} ($\varepsilon \approx {}^1/_2\ \varepsilon_{max}$) and a shoulder at ca. 22600 cm^{-1} ($\varepsilon \approx {}^1/_3\ \varepsilon_{max}$). Thus, it seems possible that with the aid of complex formation, even the study of different enol(ate) and keto tautomers in solvents of different polarities and proticities is possible. As might have been expected, the Cu^{II} complex is non-fluorescent in acetonitrile (and also in ethanol).]

Stabilities of the Complexes

Analyzing titrations of $BP(OH)_2$, BPOH, and bipy with Zn^{II} in the three solvents studied, the apparent complex stability constants determined support the conclusions drawn on the basis of the photophysical properties.

In water, BPOH and $BP(OH)_2$ yield comparable log K^{app} values of 4.1 and 4.2 and the value for Zn^{II}/bipy amounts to 4.9. The particular behaviour of BPOH in ethanol is well-reflected by the shape of the titration curve monitored at 360 nm (Figure 6, middle section), while in acetonitrile the similarity of the Zn^{II}/bipy and Zn^{II}/BPOH complexes is evident. Furthermore, whenever *N*,*O*-chelation occurs, it is not only the work necessary for desolvation of the cation and ligand and the enthalpic and entropic contributions gained by complex formation that have to be considered, but the work necessary for deprotonation also becomes important. Since we determined the apparent (spectroscopic) complex stabilities here, further investigations are necessary to study the effect of the different solvents on the true log K_1 for the reaction $M + L \rightleftharpoons ML$ (see, e.g., ref.[47]).

oPP

As mentioned above, only very small cation-induced effects on the photophysical properties of oPP were found in the course of these investigations. This is consistent with results reported previously in the literature, where oPP was described as being non-fluorescent at room temperature[24] and the only complexation reaction in water to yield spectroscopic effects was found to be that involving Be^{II} ions.[27] Besides Kábrt and Holzbecher, Johnston and Freiser reported on the complexation of oPP with Cu^{II} in water/dioxane (50:50), but for all the *o*-(2-heterocycle)phenol derivatives (with heterocycle = pyridyl, imidazolinyl, benzimidazolyl, isoquinolinyl) investigated by these researchers, the stability constant obtained for oPP was the smallest.[26] In the crystalline state, the strong internal hydrogen bond (oPP shows the shortest N−O distance in X-ray structures of the *o*-hydroxy bipyridyls)[24] represents a counterforce to the conformation oPP has to adopt in all the complexes synthesized to date (e.g. a twist of ca. 25° between the aryl rings in a Co^{III} complex,[48] and of 34° in a $[Ru^{II}bipy_2oPP]$ complex[30]). Furthermore, for the Co^{III} complex of oPP, Ganis et al. observed a broad distribution of twist angles (22−29°) for the ligand in the crystalline state, suggesting that in the complex oPP has a low rotational energy barrier.[48] In accordance with our observations, this could point to the formation of a (loose) complex in solution, which is spectroscopically inaccessible.

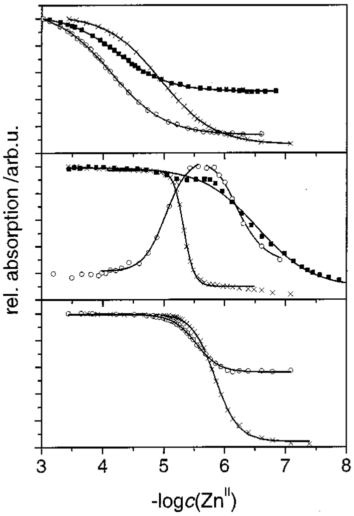


Figure 6. Titration curves [$A(\lambda)_{norm}$ vs. $-\log c_{Zn}$] for $BP(OH)_2$, BPOH, and bipy with Zn^{II} in water (top), ethanol (middle), and acetonitrile (bottom); $BP(OH)_2$ = ■, monitored at 365 nm (H_2O) and 370 nm (EtOH); BPOH = ○, monitored at 371 nm (H_2O), 360 nm (EtOH), and 335 nm (MeCN); bipy = ×, monitored at 307 nm (H_2O), 307 nm (EtOH), and 305 nm (MeCN); solid lines represent fits according to the procedure described in the Experimental Section; because of the strong overlap of the bands of the two complexes involved in a titration of $BP(OH)_2$ with Zn^{II} in MeCN, the comparatively low complex stability of these complexes, and the limited solubility of $Zn(ClO_4)_2$ in MeCN, these data are omitted in the bottom graph for better clarity

NMR Spectroscopy in Acetonitrile

In order to verify the chelate structures anticipated for $M^{II}/BP(OH)_2$ in polar solvents, the ^1H NMR spectra of $BP(OH)_2$, BPOH, and bipy, as well as their Zn^{II} and Cd^{II} complexes were recorded in deuterated acetonitrile (CD_3CN). The data are collected in Table 4.

Table 4. ^1H NMR chemical shifts (ppm from TMS) of the heteroaromatic protons of $BP(OH)_2$, BPOH, and bipy (solvent = CD_3CN, counterion = perchlorate, $c_L = 1\cdot10^{-4}$ M, $c_{Zn} = 2\cdot10^{-3}$ M, c_{Cd} = 0.185 M)

	Position							
	3	4	5	6	3′	4′	5′	6′
bipy	8.410	7.875	7.371	8.647	−	−	−	−
+ Zn^{II}	8.492	8.314	7.828	8.793	−	−	−	−
+ Cd^{II}	8.491	8.262	7.800	8.721	−	−	−	−
BPOH	−	7.304	7.292	8.184	8.564	8.014	7.451	8.575
+ Zn^{II}	−	7.819	7.669	8.386	9.072	8.259	7.746	8.794
+ Cd^{II}	−	7.769[a]	7.624[a]	8.266[a]	9.1[b]	8.188	7.702	8.691
$BP(OH)_2$	−	7.441	7.385	8.116	−	−	−	−
+ Zn^{II}	−	7.472	7.409	8.131	−	−	−	−
+ Cd^{II}	−	7.54	7.540	8.140	−	−	−	−

[a] Broad. − [b] Very broad.

An important feature with regard to the determination of the nature of the complexes is the presence and position of the signal due to the OH group involved in internal hydrogen-bond formation (Scheme 2). For the free ligands, this signal was found at the expected low field position, i.e. at $\delta = 14.14$ for BPOH and at $\delta = 14.51$ for $BP(OH)_2$. In the case of BPOH, addition of Zn^{II} ions led to a drastic shift in the position of this signal such that it appeared at $\delta = 9.22$. In contrast to this observation, the signal remains at $\delta = 14.5$ in $Zn^{II}/BP(OH)_2$, although it is broadened. Thus, the "proton chelate" in BPOH is "cracked" upon Zn^{II} complexation, but remains at least partially intact in $Zn^{II}/BP(OH)_2$ (case A in Scheme 1; see ref.[45] and, concerning the effects of internal hydrogen bonding, cf. the ^{15}N and ^{17}O NMR studies by Sitkowski et al.[49]).

The same conclusion could be drawn from the changes in the chemical shifts of the signals of the heteroaromatic protons. It is well-known that upon complexation the conformation of bipy changes from its favoured *trans* form in inert solvents to the corresponding *cis* form in the complex (bidentate chelate).[50,51] Although complex formation with bipy is accompanied by only minor changes in chemical shifts,[51,52] the downfield shifts of the 4-H and 5-H signals are especially characteristic.

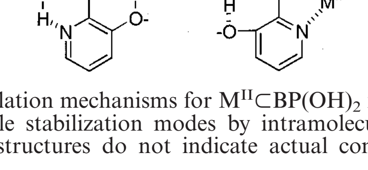
For BPOH, these shifts are of the same magnitude as for bipy (Table 4 and Figure S4, Supplementary Material). This result further supports the explanation that Zn^{II} is bound by BPOH in acetonitrile through *N,N′*-coordination with accompanying loss of the intramolecular hydrogen bond of the ligand. On the other hand, for $BP(OH)_2$, virtually no changes in the positions of the resonances of the aromatic protons are observed upon complexation. The signals are merely broadened due to the dynamics of exchange effects. This broadening is even more pronounced in the Cd^{II} complex, although the effects induced by both ions are similar (Table 4).

Unfortunately, due to the relatively high concentrations required for the NMR measurements and the rather poor solubility of Zn^{II} salts in acetonitrile, it was not possible to identify the proposed *N,N′*-chelate at high excess of Zn^{II} over $BP(OH)_2$ (see above). In the case of Cd^{II}, no such complex was observed in any experiment.

Five- vs. Six-Membered Chelates and the Influence of "Proton Chelates"

For some combinations of solvent, ion, and ligand [notably for protic solvents, Cd^{II}, and $BP(OH)_2$], the chelation behaviour found for the *o*-hydroxy bipyridyls is characterized by two unusual complexation features: (i) the formation of a six-membered ring in spite of the fact that the five-membered ring is usually more stable, and (ii) a preference for *N,O*-chelation over *N,N′*-chelation of "soft" or "borderline"[5,44] metal ions. These ions usually prefer coordination by π-donating (heterocyclic) nitrogen atoms to that by σ-donating oxygen atoms.[5]

In the case of $BP(OH)_2$, the chelate with a five-membered ring, which represents the only possible structure for $M^{II}\subset$bipy, is only favoured to some extent in solvents possessing no H-bond donating ability, e.g. acetonitrile. Only in such solvents does the possibility of forming the relatively unstable seven-membered "proton chelate" (case B in Scheme 3) with an intramolecular O−H−O bridge exist. Its formation or otherwise could not be clarified in this work. All attempts to grow crystals of this complex species were unsuccessful and the observation of a characteristic signal at $\delta \approx 18$ (O−H−O bridge)[45] in the ^1H NMR spectra was not possible due to the limited solubility of Zn^{II} salts in acetonitrile. Thus, the fact that the stability of hydrogen bond bridges ("proton chelate") is greatly enhanced for six-membered rings as compared to five- or seven-membered rings seems to be the main driving force here.[37,42,43] The strong seven-membered "proton chelate" reported by Cargill Thompson et al. for a mononuclear $Ru^{II}bipy_2{-}BP(OH)_2$ complex[45] seems to be the weaker structure in the present complexes. It is mainly the increase in mesomeric stabilization and resonance in the six-membered ring (higher degree of aromaticity) that renders the hydrogen bond stable in six-membered rings and accounts for this structural preference. The stabilizing mesomeric effect in the *N,O*-chelate can be rationalized as a "tautomeric electron-pair shift" leading to enhanced electron delocalization. Stabilization of six-membered metal ion chelates by six-membered "proton chelates" has been observed previously.[53] Furthermore, for six-membered chelates in azomethine derivatives, only minor differences between the "proton chelate" and the metal ion chelate have been observed, i.e. it is mainly the lone electron pair on the nitrogen atom that takes part in coordination and the aromatic ring π-electrons are little involved in the binding of the metal ion.[54] Here again, six-membered "proton chelates" are the most stable.[37,38] Moreover, all the observations of enhanced stability of six-membered chelates listed above have been made for systems in aqueous solutions. In the case of the *N,N′*-chelated $Ru^{II}bipy_2{-}BP(OH)_2$ complex described by Cargill Thompson et al., the limited possibilities in an $Ru^{II}bipy_2$-prearranged coordination sphere seem to favour deprotonation and *cis* chelation of $BP(OH)_2$ as the third ligand. Unfortunately, the low solubility of Zn^{II} in acetonitrile prevented the estimation of both the fluorescence quantum yield and lifetime of the 1:1 $Zn^{II}\subset BP(OH)_2$ complex, thus making a further verification of the conformation of the ligands impossible here. [Note that, as compared to the planarity of the type of chelate reported by Cargill Thompson et al., *N,N′*-chelation of $BP(OH)_2$ without deprotonation of a hydroxy group would lead to steric crowding of the OH groups and distortion of ligand planarity, resulting in blue-shifted spectra and a change in the rate constant, as has been observed for complexes of 3,3′-dimethyl-2,2′-bipyridyl.[55]]



Scheme 3. Chelation mechanisms for $M^{II}\subset BP(OH)_2$ formation, including possible stabilization modes by intramolecular hydrogen bonding (the structures do not indicate actual complex stoichiometries)

The results obtained for BPOH support the findings for $BP(OH)_2$. Even this ligand, for which *N*,*N′*-chelation should be more easily achievable owing to reduced steric hindrance (due to the lack of one *o*-hydroxyl group), favours *N*,*O*-chelation in aqueous solutions and for the primarily formed ML_2 complexes in ethanol. The formation of an additional "proton chelate" is not possible, but (a) solvent molecule(s) can saturate the second pyridyl nitrogen atom by hydrogen bonding [in the hydroxy bipyridyls where negative charge can be transferred from the oxygen to a nitrogen atom (Scheme 2), the pyridyl nitrogen atoms are more strongly π-basic]. In agreement with the solvent-dependent spectroscopic results, the only slightly smaller log K^{app} value for $Zn^{II}\subset$BPOH as compared to $Zn^{II}\subset BP(OH)_2$ in water suggests that in the latter the stabilization by the remaining intramolecular hydrogen bond is of a very delicate nature.

For the fluorescent complexes, a comparison of k_f and k_{nr} for $M^{II}/BP(OH)_2$ with those for the free ligand reveals that the stability of the planar ligand is increased in the complex, resulting in comparable rate constants for fluorescence deactivation (Table 1 cf. Table 3) but reduced rate constants for non-radiative deactivation. Thus, k_{nr} of the complexes is even smaller than that of the free ligand in apolar solvents such as *n*-hexane. The similarity of the photophysical properties of the "mono-enolate complex" $M^{II}\subset$BPOH to those of $M^{II}\subset BP(OH)_2$ in water (and to some extent in ethanol) and the completely different behaviour of most M^{II}/oPP complexes suggests that the second pyridyl nitrogen atom (and not necessarily the whole PT site) may be important with regard to stabilization in both the ground and excited states in this medium. As for $BP(OH)_2$, upon charge-transfer in the excited state, the charge density on both nitrogen atoms was found to increase for BPOH and oPP.[12,13,24]

The stronger tendency of Cd^{II} to form six-membered *N*,*O*-chelates is in agreement with results obtained by other researchers on Cd^{II} and Zn^{II} complexes of mixed *N*,*O*-containing macrocyclic ligands.[56] Here, the tendency for exclusive *N*-coordination is generally higher for Zn^{II} than for Cd^{II}.[56]

Correspondingly, the observed drastic decrease in fluorescence intensity in the complexes with paramagnetic ions is due to the formation of a stable non-fluorescent complex, i.e. static quenching occurs.[57] Complexation of Hg^{II} results in the same static quenching effect, only in this case the heavy atom effect accounts for a higher intersystem crossing rate. For none of the quenching cations could complex-specific decay components with a fluorescence lifetime >100 ps be detected with the experimental set-up employed.

Conclusion

Investigations of the complexation behaviour of $BP(OH)_2$ and BPOH in aqueous, alcoholic, and acetonitrile solutions have revealed that the heavy and transition metal ion binding properties of $BP(OH)_2$ are rather non-selective and that chelation-induced fluorescence enhancement is only observed for the d^{10} metal ions Zn^{II} and Cd^{II}. Upon complexation to Hg^{II} or paramagnetic ions, static quenching occurs. Two different chelates of the Zn^{II} and Cd^{II} complexes of the *o*-hydroxy bipyridyls have been characterized by means of solvent-dependent optical spectroscopic and NMR studies. Here, the preference for *N*,*N′*-coordination over *N*,*O*-coordination increases with decreasing proticity of the solvent in the order water < ethanol < acetonitrile and is more pronounced for Zn^{II} than for Cd^{II} as well as for the complexes of BPOH compared to those of $BP(OH)_2$. The photophysical data of the *N*,*N′*-chelates of both hydroxy-substituted ligands are very similar to those of the *N*,*N′*-chelated reference complexes $M^{II}\subset$bipy. Thus, by controlling the proticity or hydrogen-bond donating ability of the environment in particular, it is possible to direct metal ion binding along a certain path to yield specifically coordinated complexes with multifunctional ligands.

Experimental Section

Materials: $BP(OH)_2$ (98%+, purchased from Aldrich and showing essentially the same features as a freshly prepared sample[58] kindly provided by Prof. H. Langhals, Ludwig-Maximilians-Universität München), bipy (99%+, Aldrich), as well as BPOH and oPP (both gifts from Dr. F. Vollmer, Technische Universität Berlin, synthesized according to ref.[24]) were checked by TLC (Kieselgel F_{254}, Merck) and used as received. Stock substrate solutions, typically $1\cdot10^{-3}$ M (in acetonitrile and ethanol) or $5\cdot10^{-5}$ M (in water), were kept under nitrogen and stored in the dark at 4 °C. Metal perchlorates purchased from Merck, Acros, or Aldrich were of the highest available purity and were dried (vacuum oven) to a definite water content employing various procedures adapted from ref.[59] For example, Hg^{II} perchlorate was dried at 75 °C for 12 h yielding $Hg^{II}(ClO_4)_2\cdot 3\,H_2O$, while $Zn^{II}(ClO_4)_2\cdot 2\,H_2O$ was obtained by drying the commercial product at 100 °C in vacuo for 12 h. Stock solutions, typically $1\cdot10^{-3}$ to 0.1 M (depending on the solubility of the metal salt in the relevant solvent), were stored under nitrogen in the dark at 4 °C (**Caution**: Perchlorate salts present a potential explosion hazard and should be handled with care and possibly only in small quantities!). Ethanol and acetonitrile (Aldrich) were of UV-spectroscopic grade. Doubly-distilled water (pH 6.39) was provided by the Laboratory for Trace Elemental Analysis, BAM, Berlin.

Steady-State Absorption and Fluorescence Spectroscopy: UV/vis spectra were recorded on a Carl Zeiss Specord M400/M500 absorption spectrometer, while steady-state emission spectra were measured with a Perkin−Elmer LS50B and a Spectronics Instruments 8100 spectrofluorometer. To determine the relative fluorescence quantum yields (φ_f), the optical densities (OD) of the solutions at the excitation wavelengths were adjusted to 0.1 ± 0.001 in 100 mm absorption cells. These solutions were then transferred to a 10 mm quartz cell and the fluorescence measurements were performed with a standard 90° geometry and with excitation and emission polarizers set at 0° and 54.7°. Quinine sulfate dihydrate (NIST standard reference material SRM 936) in 0.1 N H_2SO_4 ($\varphi_f = 0.51 \pm 0.03$)[60] and $BP(OH)_2$ in cyclohexane ($\varphi_f = 0.31 \pm 0.02$)[12b] were used as fluorescence standards. All fluorescence spectra presented here have been corrected for the spectral response of the detection system (calibrated quartz halogen lamp placed inside an integrating sphere; Gigahertz-Optik) and for the spectral irradiance of the excitation channel (calibrated silicon diode mounted at a sphere port; Gigahertz-Optik). The fluorescence quantum yields were calculated from 4 independent measurements; the uncertainties in the measurements were estimated to be ±5% (for $\varphi_f > 0.2$), ±10% (for $0.2 > \varphi_f > 0.02$), ±20% (for $0.02 > \varphi_f > 5\cdot10^{-3}$), and ±30% (for $5\cdot10^{-3} > \varphi_f$), respectively.

Time-Resolved Fluorescence Spectroscopy: Fluorescence lifetimes (τ_f) were measured with synchrotron radiation from the Berlin Storage Ring for Synchrotron Radiation (BESSY).[61] The fluorescence was collected at right angles (monochromators with a spectral bandwidth of 8 nm) and the excitation wavelength of the synchrotron radiation was selected with a monochromator of 2 nm spectral bandwidth. The pulsed excitation source BESSY allowed for a temporal resolution of 100 ps (single-bunch mode; 4.8 MHz). The fluorescence decay curves were recorded with a time-correlated single-photon counting set-up and a time division of 55.5 ps channel^{-1}; typical count rates were of the order of $1\cdot10^3$ counts s^{-1}. For the fluorescence decay measurements, data were accumulated up to 5000 counts in the peak channel for a single decay. The temporal calibration of the experimental set-up for the time-resolved measurements was checked with Rose Bengal in methanol ($\tau_f = 0.50 \pm 0.02$ ns),[62] 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) in ethanol ($\tau_f = 1.35 \pm 0.20$ ns),[63] and fluorescein 27 in 0.1 N NaOH ($\tau_f = 4.50 \pm 0.03$ ns).[63] For all the decay measurements, emission polarizers were set at 54.7°.

NMR Spectroscopy: One- and two-dimensional NMR spectra [COSY (90°) and ^{13}C/^{1}H HECTOR] were recorded on a Bruker DMX 400 spectrometer (5 mm tube, CD_3CN, deuterium lock). The ^{1}H NMR spectra of the free ligands were assigned on the basis of the typical coupling patterns for such compounds. In particular, the signals due to 6-H (α to the pyridyl nitrogen atom), showing a decreased vicinal coupling constant ^{3}J(5-H, 6-H),[64] were easily identified. Application of the method of incremental schemes,[64] well-established for pyridyl systems, revealed a good agreement between the measured and tabulated data and the coupling constants obtained correspond well with data reported for pyridyl systems in the literature.[64] In the case of BPOH, additional measurements were necessary to fully assign all the seven ^{1}H signals. A two dimensional ^{1}H-^{1}H correlation spectrum (COSY) allowed the separation of the three-spin system of the hydroxypyridyl moiety and the four-spin system of the pyridyl ring. The close similarity of the 4-H and 5-H signals (AB part of an ABX spectrum) and of the 3′-H and 6′-H signals could be resolved by means of hetero-correlated ^{13}C-^{1}H spectra (partly including ^{1}H-^{1}H homo-coupling).

Complex Stability Constants: The complex stability constants K reported herein were determined from absorption measurements (in 50 or 100 mm absorption cells) by adding aliquots of the appropriate metal ion solution to a solution of the ligand (c_{M0} titration). Besides large errors encountered in absorption (or fluorescence) measurements at (very) low ligand concentrations (very dilute solutions), the solubility of the ligands (especially in water and when a high excess toward the end of the titration is required) proved to be the limiting factor for performing c_{L0} titrations in order to determine K values of high order (1:2, 1:3 complexes) or successive K_n values. The latter was also hampered by the spectral similarities of the individual complexes. In the case of high complex stability constants [e.g. for complexes of $BP(OH)_2$ with paramagnetic ions] as well as mixed stoichiometries, fitting of the c_{M0} titration data to 1:1 and 1:2 complexes yielded no K_n values of acceptable accuracy. Thus, in order to obtain a measure for all the cations investigated, the apparent complex stability constant K^{app} was obtained by carrying out c_{M0} titrations with similar c_{L0} and fitting the sigmoidal curve of a $\Delta A(\lambda)$ vs. $-\log c_M$ plot. When no diverse spectral features occur in such a c_{M0} titration, K^{app} corresponds best to the process $M + ML_2 \rightarrow 2\ ML$.

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