Zinc and cadmium complexes with an achiral symmetric helicand. Crystal structure of an enantiomerically pure Λ-Zn(II) monohelicate

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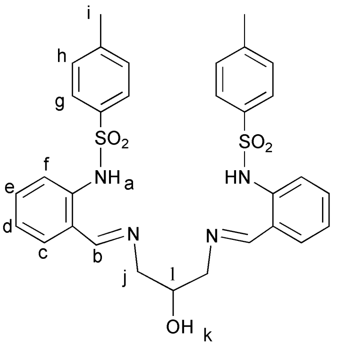
Zn(II) and Cd(II) complexes with an *N*-tosyl substituted N_4-donor Schiff base, containing a 2-propanol residue as spacer, have been prepared. The X-ray crystal structure of the monohelicate Λ-Zn(OHPTs)·H_2O [H_2OHPTs: *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-diamino-2-propanol] has been solved. The Zn(II) ion assumes a distorted tetrahedral coordination geometry, involving the four donor N atoms of the bisdeprotonated ligand. Strong (O–H···O) hydrogen bonds between neighbouring complex and lattice water molecules lead to intricate intermolecular interactions that seem to drive the crystal packing. This Zn(II) complex shows an intense blue fluorescence in solution ($\lambda = 430$ nm, $\phi = 0.14$), which is also observed in the solid state ($\lambda = 490$ nm). Cd(OHPTs)·$4H_2O$, although at a lower level ($\phi = 0.08$), is also luminescent ($\lambda = 430$ nm) in acetonitrile solution.

Enantiopure compounds are of central importance in many domains of chemistry.[1] The obtention of helical complexes,[2,3] which are intrinsically chiral, has significantly contributed to their development in the last years. Enantiopure ligands[4] are employed to induce stereoselectivity, or even stereospecificity, and so provide enantiomeric excesses of the *P* or *M* metallohelicates.[3] Achiral ligands yield racemic mixtures of self-assembled *P* and *M* helixes, although in exceptional cases, crystallisation allows their spontaneous resolution.[5] Chromatographic techniques[6] or resolving agents[7] can be also employed to resolve racemates.

General construction principles involved in the preparation of helical complexes have been widely studied.[2–4,8] Now, it is known that the spacer group between the metal binding domains is a key element in the formation and even in the microarchitecture of metallo-helicates. Moreover, hydrogen bonds and other weak interactions,[9] such as face-to-face or edge-to-face π-stacking,[10] are frequently responsible for the construction of supramolecular motifs.

In recent years, we have been working with *N*-tosyl substituted N_4-donor diimines containing two- or three-membered spacers.[11,12] We have found that a ligand of this type containing a $(CH_2)_3$ alkyl spacer can act as a N_4-tetradentate ligand with Cd^{2+} and as a bis(N_2-bidentate) one with Zn^{2+} ions, yielding both mono- and double helical metal complexes, respectively.[11a]

Here, we would like to explore how the ability of a CH_2–CH(OH)–CH_2 spacer to form hydrogen bonds, can influence the spatial arrangement of *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-diamino-2-propanol (H_2OHPTs, Scheme 1) in its zinc and cadmium complexes. Additionally, the study of some photophysical properties of the ligand and its complexes has also attracted our attention, since another Zn(II) complex containing this type of diimine, but with a 1,2-diaminocyclohexane residue as spacer, was fluorescent.[12a] In this case, the presence of a hydrogen bonding site, such as the OH group, could enhance the fluorescence emission.[13]



Scheme 1 Schematic representation of H_2OHPTs and labelling scheme for ^{1}H NMR studies.

Experimental

Materials and methods

Chemicals of the highest commercial grade available (Aldrich) were used as received. Zinc and cadmium metal plates (Aldrich) were washed with a dilute hydrochloric acid solution prior to electrolysis.

Elemental analyses were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on Bruker DPX-250 and DRX-500 spectrometers, using acetonitrile-d_3 as solvent. Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. Mass spectra (FAB) were recorded on a Micromass Autospec spectrometer, employing *m*-nitrobenzyl alcohol as matrix. UV absorption spectra were recorded on a Perkin–Elmer Lambda 6 spectrophotometer, and fluorescence emission spectra on a SPEX F111 Fluorolog spectrofluorimeter. All measurements were carried out at room temperature and in the presence of air.

Fluorescence emission spectra in the solid state were recorded as KBr pellets or thin films. These were obtained by slow evaporation of saturated compound solutions ($CHCl_3$) on a quartz cell. UV and fluorescence studies in solution were carried out using 10^{-3}–10^{-5} M acetonitrile solutions. Trifluoroacetic acid (TFA) or tetrabutylammonium hydroxide was gradually added to the complex solution, and the corresponding spectra were recorded.

Ligand synthesis

N,*N*′-Bis(2-tosylaminobenzylidene)-1,3-diamino-2-propanol, H_2OHPTs, has been prepared by condensation of 2-tosylaminobenzaldehyde[14] (5.0 g, 18.16 mmol) with 1,3-diamino-2-propanol (0.82 g, 9.1 mmol). A chloroform solution (150 cm^3) was heated at reflux over a 4 h period and subsequently concentrated *in vacuo*. The yellow precipitate formed was collected by filtration, washed with diethyl ether (30 mL), and dried *in vacuo*.

H_2OHPTs. Yellow solid. Yield 4.8 g (88%); mp 161 °C; Anal. found: C, 61.65; H, 5.41; N, 9.33; S, 10.48. Calcd. for $C_{31}H_{32}N_4O_5S_2$: C, 61.56; H, 5.29; N, 9.27; S, 10.60%. IR (KBr, cm^{-1}): ν(O–H) 3510(b), ν(N–H) 3363(b), ν(C=N) 1639(s), ν(C–N) 1337(s), $\nu_{as}(SO_2)$ 1287(s), $\nu_s(SO_2)$ 1159(s); FAB MS (*m*/*z*): 605.3 (100%, M^+). UV (MeCN, nm): 221(vs), 262(sh), 310(w). Fluorescence (solid state, nm): 369(vw).

Metal complexes

Caution! *Although no problems have been encountered in this work, all perchlorate compounds are potentially explosive, and should be handled in small quantities and with great care!* Complexes have been obtained by an electrochemical method[11,12] in which a metal anode was oxidised in an acetonitrile solution of H_2OHPTs. The preparation of Zn(OHPTs)·$4H_2O$ is outlined below. The cell can be summarised as: $Zn_{(+)}|H_2OHPTs + NMe_4ClO_{4(MeCN)}|Pt_{(-)}$. An acetonitrile solution (80 cm^3) of H_2OHPTs (100 mg, 0.165 mmol), containing about 20 mg of tetramethylammonium perchlorate, was electrolysed for 1.75 h using a 5 mA current intensity and a initial voltage of 12.8 V. Filtration and concentration of the resulting solution to a third of its initial volume yielded a solid that was washed with diethyl ether and dried *in vacuo*. The ligand amount, current intensity and electrolysis time are identical for both M(OHPTs)·$4H_2O$ (M = Zn and Cd). Initial voltage was 9.4 V for the Cd(II) complex.

Zn(OHPTs)·$4H_2O$. Brownish solid. Yield 0.089 g (73%). Anal. found: C, 49.87; H, 5.08; N, 7.46; S, 8.78. Calcd. for $C_{31}H_{38}N_4O_9S_2Zn$: C, 50.30; H, 5.18; N, 7.57; S, 8.66%; IR (KBr, cm^{-1}): ν(O–H) 3444(b), ν(C=N) 1641(s), ν(C–N) 1291(s), $\nu_{as}(SO_2)$ 1263(s), $\nu_s(SO_2)$ 1138(s). FAB MS (*m*/*z*): 667.3 (3%, $M^+ - 4H_2O$). UV (MeCN, nm): 232(vs), 273(sh), 347(w). Fluorescence (MeCN, nm): 430(vs), (solid state, nm) 490(vs).

Cd(OHPTs)·$4H_2O$. Yellow solid. Yield 0.091 g (70%). Anal. found: C, 46.97; H, 4.92; N, 7.08; S, 8.23. Calcd. for $C_{31}H_{38}CdN_4O_9S_2$: C, 47.29; H, 4.87; N, 7.12; S, 8.14%; IR (KBr, cm^{-1}): ν(O–H) 3435(b), ν(C=N) 1636(s), ν(C–N) 1288(s), $\nu_{as}(SO_2)$ 1258(s), $\nu_s(SO_2)$ 1122(s). FAB MS (*m*/*z*): 717.1 (4%, $M^+ - 4H_2O$). UV (MeCN, nm): 237(vs), 268(sh), 341(w). Fluorescence (MeCN, nm): 430(s).

Single crystal X-ray diffraction studies

The structure determination was performed at room temperature on a Siemens CCD Diffractometer, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares based on F^2, using SHELX-97 software.[15] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at geometrically calculated positions with thermal parameters derived from the parent atoms, except those bonded to the water molecule. These could be located in the difference map and included at these sites, with a fixed isotropic displacement factor of $U = 0.1$ Å^2, without further refinement. Table 1 provides a summary of crystal data, data collection and refinement parameters. Molecular graphics are represented by Ortep-3 for Windows.[16]

Table 1 Crystal and structure refinement data for Λ-Zn(OHPTs)·H_2O

Empirical formula	$C_{31}H_{32}N_4O_6S_2Zn$
M	686.10
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	9.127(3)
b/Å	16.830(3)
c/Å	20.558(5)
U/Å^3	3157.9(15)
T/K	298(2)
Z	4
μ(Mo-Kα)/mm^{-1}	0.959
Reflections collected	21160
Independent reflections	7757
R_{int}	0.1065
R_1 [$I > 2\sigma(I)$]	0.0545
wR_2 [$I > 2\sigma(I)$]	0.1046
R_1 (all data)	0.1165
wR_2 (all data)	0.1208

CCDC reference number 191646. See http://www.rsc.org/suppdata/nj/b2/b201433p/ for crystallographic files in CIF or other electronic format.

Results and discussion

Single crystal X-ray diffraction studies

Slow evaporation of a saturated Zn(OHPTs)·$4H_2O$ acetonitrile solution yielded dark brown crystals of Zn(OHPTs)·H_2O suitable for X-ray diffraction studies. The crystallographic analysis shows that the asymmetric unit consists of a discrete molecule of Zn(OHPTs) and a solvated water molecule. The molecular structure of the single-stranded (*M*)-helical complex is represented in Fig. 1, with the atom labelling scheme used in Table 2, which lists the most relevant bond distances and angles.

The zinc(II) ion is tetra-coordinated to the four N atoms of the Schiff base ligand and consequently, it can be considered as saturated[3a] since the Schiff base fulfils its stereochemical requirements. The Zn–N distances (Table 2) are in the usual range reported for this type of complex.[11a,17] Likewise, the Zn–N_{imine} distances are slightly longer than the Zn–N_{amide} ones, as occurs in a related [4 + 4] bishelical Zn(II) complex.[11a] One of the O atoms of each tosyl group [O(2) and O(5)] is weakly bonded to the metal ion. These Zn···O distances (about 2.7 Å) are too long to be considered as true coordinated bonds. Thus, the coordination environment can be regarded as pseudo-tetrahedral, as the dihedral angle θ between both N–Zn–N terminal planes is *ca.* 68.33°.

The central six-membered chelate ring formed by the spacer shows a non-planar arrangement in accordance with its alkylic nature. Its least-squares calculated plane forms angles of 49.12° and 53.01° with both terminal chelate planes, which is indicative of a helical ligand arrangement. If only the donor atoms are considered, the ligand does not complete a twist

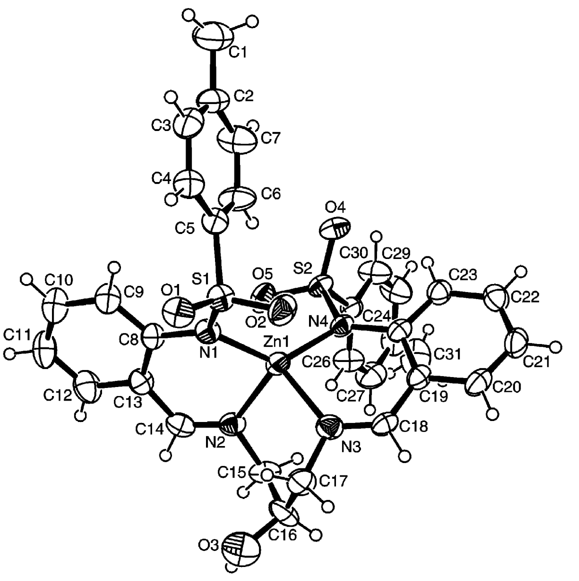


Fig. 1 ORTEP view of Λ-Zn(OHPTs). Ellipsoids are drawn at 40% probability.

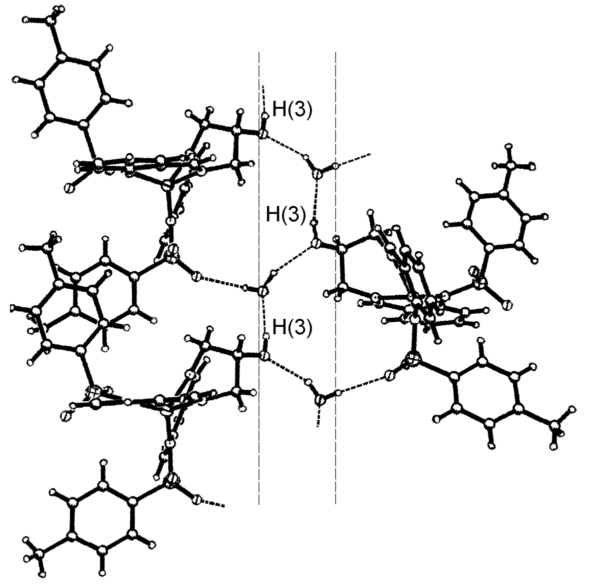


Fig. 2 Intermolecular O–H···O interactions between solvated water and three molecules of Λ-Zn(OHPTs)·H_2O. All of them occur in a channel indicated by the dashed lines.

around the metal centre (*ca.* 260°). However, if we consider the whole ligand, the tosyl groups slightly exceed a 360° turn, as occurs in other related monohelicates.[11a,12a] The S(1)···S(2) distance (*ca.* 4.82 Å) in Zn(OHPTs)·H_2O is used to quantify the helical pitch.

The OH group on the spacer of Zn(OHPTs)·H_2O seems to be of the utmost importance, since the ligand without this hydroxyl group on the spacer, PTs^{2-}, yields a Zn(II) [4 + 4] bishelicate.[11a] The explanation of this unusual behaviour is not simple, so we have considered below some factors that could be influential.[9,10]

Hydrogen bonding. The OH group is interacting *via* H(3) with the solvated water molecule present in the asymmetric unit. The latter is simultaneously connected to the OH group of a second complex molecule and to a third one, through an O atom of one tosyl group. All of these interactions occur along a narrow channel (Fig. 2), formed by tosyl and hydroxyl groups of facing stacks of complex molecules that can so trap water molecules. Hydrogen bonding could play a role in autoresolution.[9b]

Table 2 Selected bond distances and angles for Λ-Zn(OHPTs)·H2O

Zn(1)–N(4)	1.968(3)			
Zn(1)–N(1)	1.985(4)			
Zn(1)–N(3)	2.035(4)			
Zn(1)–N(2)	2.042(4)			
N(1)–Zn(1)–N(2)	91.26(16)			
N(2)–Zn(1)–N(3)	87.62(16)			
N(3)–Zn(1)–N(4)	91.03(15)			
N(1)–Zn(1)–N(3)	128.29(16)			
N(1)–Zn(1)–N(4)	130.17(15)			
N(2)–Zn(1)–N(4)	123.54(16)			
N(2)–C(15)–C(16)–C(17)	−37.4(6)			
C(15) C(16) C(17) N(3)	−36.1(6)			
H bonds				
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	⟨(DHA)
O(3)–H(3A)···O(1S).	0.82	1.98	2.788(7)	168.2
O(1S)–H(1SA)···O(1)^1	0.85	2.14	2.968(6)	163.2
O(1S)–H(1SB)···O(3)^2	0.85	2.12	2.913(6)	156.1

Symmetry transformations used to generate equivalent atoms: $^1x-1, y, z$; $^2x-1/2, -y+1/2, -z+2$.

Weak interactions. Many weak C–H···O interactions were detected and could be responsible for the non-equivalent conformation of the two tosyl groups in the single helicate. Likewise, some feeble C–H/π and π-π stacking interactions are present as well. These interactions are the most significant in the packing scheme[5c,10] of other related crystal structures that lack H bonding.[11,12]

Conformation of the spacer. Monohelical complexes containing $(CH_2)_n$ spacers usually arrange their methylene chains in rather regular *gauche*-only conformations.[11a] In Zn(OHPTs)·H_2O, the presence of the OH group on the central C atom clearly distorts the spacer (torsion angles lie in a 36–85° range, instead of *ca.* 60°). The OH group is almost *anti* conformed with respect to N(3) (157°) and distantly *gauche* conformed with respect to N(2) (80°). This arrangement minimises steric hindrances and could increase the racemisation barrier in solution.[18]

Zn(HOPTs)·H_2O crystallises in the chiral space group $P2_12_12_1$ of the orthorhombic system and consequently, all the helical molecules show the same handedness. Refinement of the Flack enantiopole parameter[19] [−0.0324(14)] demonstrates that this crystal only contains the pure Λ enantiomer of the complex. Since the ligand is achiral, and so unable to induce a predetermined chirality,[2–4] Zn(HOPTs)·H_2O has undergone complete spontaneous resolution upon crystallisation.[5,20] The lack of optical activity exhibited by a crystalline sample of this Zn(II) complex in acetonitrile solution demonstrates the presence of a racemate in solution. This behaviour is typical of a conglomerate,[20] which contains equal amounts of crystals of both handednesses. The previous determination of the crystal structure of anomer enantiomerically pure Δ complex containing this type of Schiff base with Ni(II)[12b] reinforces the conglomerate hypothesis.

^{1}H NMR studies

H_2OHPTs. A NOESY experiment shows the expected couplings, those corresponding to neighbouring aromatic protons or between the hydroxyl (H_k) and methylene (H_j) protons (Scheme 1). This experiment also allows a full assignment of the ^{1}H NMR signals (Table 3) and indicates the close proximity (below 3.2 Å) between the imine (H_b), methylene (H_j) and some aromatic (H_c and H_g) protons in solution. The

Table 3 ^{1}H NMR signals (in ppm) for the free ligand and complexes using acetonitrile-d$_3$ as solvent[a]

Assignment	H_2OHPTs	Zn(OHPTs)·4H_2O	Cd(OHPTs)·4H_2O
H_a	13.26 s 2H		
H_b	8.47 s 2H	8.48 s 1H; 8.45 s, 1H	8.46 s 2H
H_g	7.75 d (8.5) 4H	7.84 d (8.5) 4H	7.87 d (8.5) 4H
H_c	7.42 d (7.5) 2H	7.47 m 4H	7.30 d (7.5) 2H
H_f	7.65 d (7.5) 2H,		7.40 d (8.0) 2H
H_e	7.35 t (7.5) 2H	7.28 m 6H	7.22 m 6H
H_h	7.25 d (8.5) 4H		
H_d	7.11 t (7.5) 2H	6.94 t (7.5) 2H	6.90 t (7.5) 2H
H_j	3.99 m 2H; 3.87 m 2H	4.36 m 2H; 3.65 m 2H	4.12 m 2H; 3.72 m 2H
H_k	4.30 b 1H	4.07 m 1H	4.22 m 1H
H_l	3.33 b 1H	3.84 m 1H	3.52 m 1H
H_i	2.31 s 6H	2.35 s 6H	2.33 s 6H

[a] Abbreviations: s: singlet; d: doublet; t: triplet; m: multiplet; b: broad. ^3J in Hz are given in parentheses.

H_b–H_g coupling reveals that H_2OHPTs could be folded in a similar conformation to that found in the solid state for a related diimine containing a C_6H_{10} spacer.[12a]

Zn(HOPTs)·H2O. The presence of two signals for H_j is coherent with the diastereotopic nature of the geminal protons in each methylene group, as a result of the helicity.[5b,21] The methylene protons ($H_{j_{eq}}$) in an equatorial position with respect to the planes C(17)–N(3)–C(18)–C(19)–C(20) or C(15)–N(2)–C(14)–C(13)–C(12) are observed at higher field than those sited near the axial positions ($H_{j_{ax}}$).

A NOESY experiment indicates the close proximity between imine, methylene and hydroxyl protons as well as between H_g, H_f, $H_{j_{ax}}$ and H_l in acetonitrile solution. This last fact seems to indicate that at least one tosyl group remains nearly perpendicular to the C(17)–N(3)–C(18)–C(19)–C(20) plane, in a similar disposition to that observed in the solid state for the Zn(II) single helicate.

COSY and NOESY experiments at room temperature clearly show the AB spin behaviour of the methylene protons on the NMR timescale. Thus, Zn(OHPTs)·H_2O does not seem to be rapidly racemising in solution, and conglomeration[20] is the most likely procedure involved in obtaining this enantiopure complex.

Cd(HOPTs)·4H_2O. The smaller separation between the $H_{j_{ax}}$ and $H_{j_{eq}}$ signals for Cd(OHPTs)·4H_2O could indicate a more planar arrangement for $OHPTs^{2-}$ in the Cd(II) complex than in the Zn(II) one. This view is reinforced by the observation of two singlet signals for the imine protons in the Zn(II) complex only, as well as the greater ionic radius of a tetracoordinated Cd(II) ion (0.92 Å) compared to a similar Zn(II) ion (0.74 Å).[22] The satellite signals allied to the main imine resonance in the Cd(II) complex spectrum are ascribed to coupling between H_b and the naturally abundant nuclei of ^{113}Cd and ^{111}Cd ($I = 1/2$). The intensities of the NMR satellites relative to the central imine singlet are 1 : 6 : 1.

UV-Vis absorption and fluorescence emission studies

The stability of H_2OHPTs and Zn(OHPTs)·H_2O in acidic acetonitrile solutions was studied by UV spectroscopy after addition of increasing amounts of trifluoroacetic acid (TFA). No aqueous solvents were used due to hydrolysis and problems with low solubility. The UV absorption of the free ligand is unaffected even at a 1 : 12 (H_2OHPTs:TFA) molar ratio. In contrast, the complex seems to suffer a demetallation reaction after reaching a 1 : 5 (complex:TFA) molar proportion. This was deduced from the appearance of the same absorption spectrum recorded for the free ligand. The demetallation hypothesis points to the reversibility of the complexation reaction, by protonation of the amide N atoms depending on the medium acidity. The observation of isosbestic points (at 225, 248, 264, 293 and 322 nm) in the UV spectra of Zn(OHPTs)·H_2O during the addition of TFA suggests the existence of different species in solution, such as H_2OHPTs, Zn(OHPTs), $Zn(HOHPTs)^+$ or $Zn(H_2OHPTs)^{2+}$. Unfortunately, additional measurements to determine the H_2OHPTs–Zn(II) interaction constant were unsuccessful, probably due to slow complexation kinetics under these acidic conditions.

H_2OHPTs presents a weak fluorescence emission in the solid state with a maximum at 369 nm that almost disappears in acetonitrile or methanol solutions. This contrasts with the intense luminescence (*ca.* 425 nm in MeCN solution at $\lambda_{exc} = 260$ nm) shown by an equivalent Schiff base ligand containing a $(CH_2)_3$ spacer.[12a] The presence of the hydroxyl group on the spacer must be responsible for the quenching phenomenon.

The chelation of Cd(II), and especially Zn(II), to $OHPTs^{2-}$ leads to an enhancement of the fluorescence emission (CHEF effect).[23] At room temperature Zn(OHPTs)·H_2O shows an intense luminescence at about 490 nm in the solid state and at 430 nm in acetonitrile solution, as its quantum yield ($\phi = 0.14$) indicates. Although the origin of the fluorescence remains unknown, the active unit could be located on the 2-tosylaminobenzaldehyde residue, since this exhibits an intense luminescence at about 498 nm in MeCN solution. Fluorescence emission by metal complexes in the solid state presents an attractive alternative to the usual inorganic materials

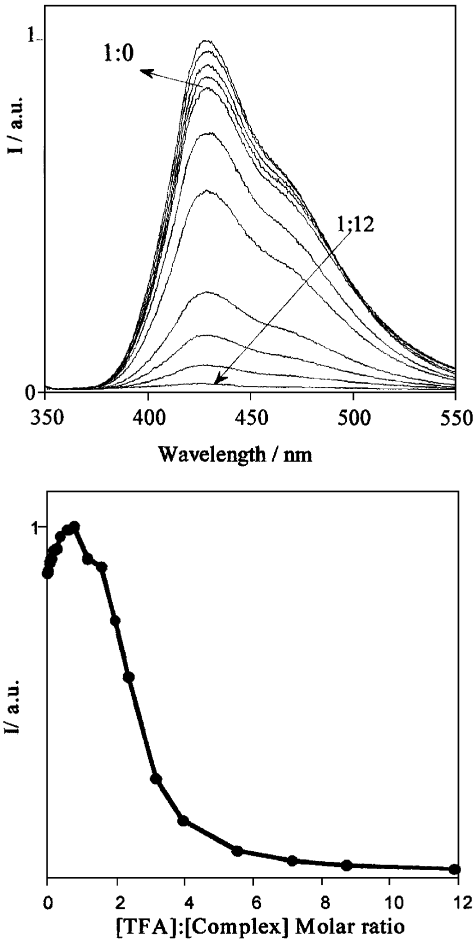


Fig. 3 Dependence of fluorescence emission intensity on added TFA for Zn(OHPTs)·H_2O (in acetonitrile solution, $\lambda_{exc} = 313$ nm) on the wavelength (top) and complex : TFA molar ratio (bottom).

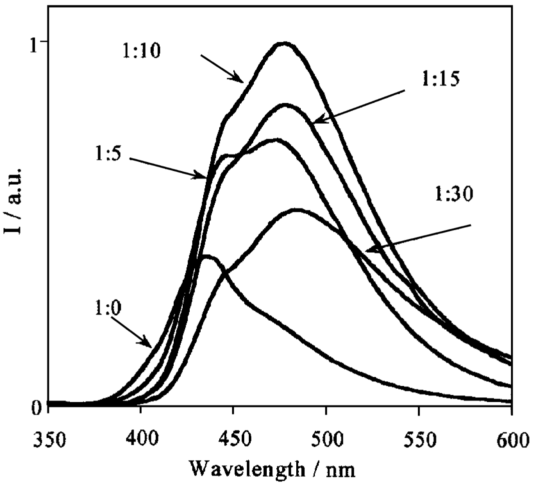


Fig. 4 Dependence of the fluorescence emission spectra ($\lambda_{exc} = 313$ nm) for $Zn(OHPTs)\cdot H_2O$ in acetonitrile solution on the complex : $NBu^n{}_4OH$ molar ratio.

employed as the active layer in light-emitting diode devices (LEDs) and lasers.[24]

The variation of the fluorescence emission with TFA can be observed in Fig. 3. The addition of acid up to equimolar amounts of complex and TFA slightly increases the fluorescence intensity. Nevertheless, after this maximum, the successive addition of acid leads to a progressive decrease of the fluorescence that finally (above a 1 : 5 molar ratio) results in a residual emission. In the case of $Cd(OHPTs)\cdot 4H_2O$ ($\phi = 0.08$) the fluorescence emission decreases to half intensity when a 1 : 1.5 complex:TFA molar ratio is reached, and it is totally quenched after increasing the molar ratio up to 1 : 5, suggesting a stability similar to that observed for the zinc complex in acid media.

Furthermore, we have studied the stability of $Zn(OHPTs)\cdot H_2O$ in alkaline solutions, when mixed with tetrabutylammonium hydroxide in 1 : 5, 1 : 10, 1 : 15, 1 : 25 and 1 : 30 ratios. UV absorption spectra are highly dependent on the amount of $NBu^n{}_4OH$ added. This study was monitored by NOESY and COSY experiments for $Zn(OHPTs)\cdot H_2O{:}ND_4OD$ mixtures with the mentioned ratios. Contrary to what was observed during the addition of TFA, addition of $NBu^n{}_4OH$ leads to a gradual shift to longer wavelength of the three characteristic UV bands. The fluorescence emission band experiences a notable intensity increase and a red-shift, after addition of $NBu^n{}_4OH$, reaching a maximum with a 1 : 10 molar ratio (476 nm). The successive addition of the base until 1 : 15, 1 : 25 and finally 1 : 30 (complex:$NBu^n{}_4OH$) molar ratios, results in a gradual fluorescence quenching, which Fig. 4 illustrates. However, this 1 : 30 mixture is still more fluorescent than the Zn(II) complex solution.

The simultaneous ^1H NMR experiments seem to indicate that after reaching a 1 : 5 molar ratio, the complex remains unaltered in solution. However, the spectra corresponding to a 1 : 10 mixture show some significant modifications, related to the appearance of new species that show an upfield shift of their aromatic signals with respect to the $Zn(OHPTs)\cdot H_2O$ spectrum. Their intensity and number progressively increase until reaching the 1 : 30 ratio, whilst the Zn(II) complex signals are still mainly observable.

Conclusions

Crystallisation of $Zn(OHPTs)\cdot 4H_2O$ occurs with spontaneous resolution to produce enantiopure crystals of Λ-$Zn(OHPTs)\cdot H_2O$. The crystal packing is based on an intricate H-bonded network among OH spacer groups, water molecules and O atoms of the tosyl groups, which form channels along the crystal.

The Zn(II) ion assumes a distorted tetrahedral coordination geometry, involving the four N atoms of the dianionic ligand. The N_4 donor ligand displays a helical conformation, in which the tosyl groups show a different spatial arrangement, that precludes its global consideration as a symmetric helicand thread. Weak intramolecular $C\text{–}H\cdots O$ interactions could be responsible for the unequal disposition of both tosyl groups in the single helicate. This asymmetric helical arrangement observed in the solid state seems to remain in acetonitrile solution.

Preliminary photophysical studies show that chelation of Cd(II), and especially Zn(II), to $OHPTs^{2-}$ leads to an enhancement of the fluorescence emission. A demetallation reaction of $Zn(OHPTs)\cdot H_2O$ seems to occur in acidic acetonitrile solution when a 1 : 5 (complex:TFA) molar ratio is reached. On the contrary, addition of $NBu^n{}_4OH$ up to a 1 : 10 (complex:alkali) molar ratio leads to a doubling of the emission intensity.

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