Zinc–salophen complexes as selective receptors for tertiary amines

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Zinc–salophen compounds **1–3** incorporating in the given order 1,2-diaminobenzene, 2,3-diaminonaphthalene, and 9,10-diaminophenantrene moieties were synthesised. Their binding properties toward a series of tertiary amines were assessed by UV-Vis and fluorescence spectroscopy in chloroform solution. Unprecedented selectivities of quinuclidine *vs.* triethylamine higher than 10^5 were recorded, thereby revealing the dramatic influence of steric effects on axial coordination of tertiary amines. X-Ray diffraction analyses showed that in the solid state compound **2** is dimeric, but its 1 : 1 quinuclidine complex is monomeric. Strong indications were obtained that both free receptors and their amine adducts are monomeric in dilute chloroform solution.

Introduction

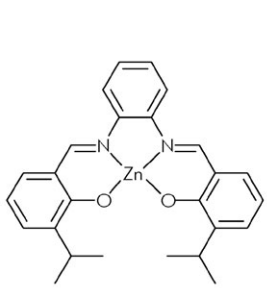
There has been a considerable increase of interest in the molecular recognition of amines in recent years. The important role played by amines in biologic[1] and environmental processes[2] has promoted the search for synthetic receptors endowed with high affinities,[3] and selectivities[4] for use in the development of chemosensors for such compounds.

Zinc–salophen complexes have attracted much attention in a number of recent structural[5–7] and catalytic[8] studies and in the construction of multicomponent supramolecular assemblies.[9] Their well known capability to accept one axially coordinated donor species, along with their photophysical properties,[10] make them suitable candidates for the development of amine receptors.[11] However, because of the paucity of quantitative data, the structural factors at work in amine binding to zinc–salophen compounds are still largely unexplored.

In this work, we describe the preparation of new zinc–salophen derivatives **1–3** and report our findings on the very surprising influence of steric effects on the binding abilities of the above compounds toward a series of tertiary amines in which the steric hindrance decreases in the order diisopropylethylamine, **4** > triethylamine, **5** > dimethylethylamine, **6** > quinuclidine, **7**. The X-ray molecular structures of compound **2** and of its 1 : 1 quinuclidine adduct are also reported.

Results and discussion

Compounds **1–3** were prepared according to the standard template procedure for salen and salophen metal complexes[5] using 3-isopropylsalicylaldehyde, zinc acetate dihydrate, and the appropriate diamino compound as starting materials. The reactants were refluxed in methanol for 1 h, during which time the desired products precipitated as yellow solids in pure form. The presence of two isopropyl groups in the *ortho* positions with respect to the phenoxide (positions 3,3′) oxygens increases the solubility in organic solvents of low polarity.



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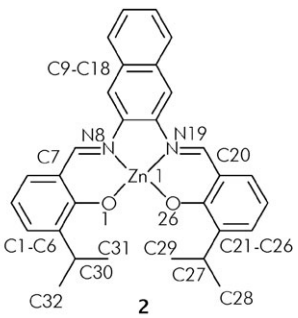

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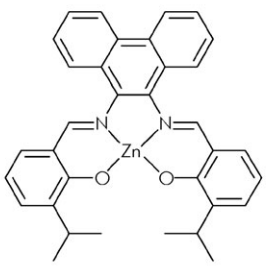

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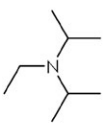

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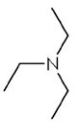

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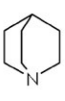

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X-Ray crystallography

Dimeric structures of zinc–salophen compounds are well documented in the literature.[5,12,13] Recently Reek and coworkers[12,13] pointed out that the presence of 3,3′-positioned *tert*-butyl groups is a prerequisite for the existence of

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monomeric species both in solution and in the solid state. In the absence of such sterically demanding substituents a strong tendency toward dimer formation through intermolecular oxygen bridges is expected. Since a dimeric zinc–salophen receptor is likely to be much less prone to amine complexation than a monomeric one, dimerization was a question of major concern in the present study.

Several attempts at crystallising the zinc–salophen compounds either alone or in the presence of their amine guests were carried out. Good quality crystals were obtained only from the crystallization of compound **2** by slow evaporation of a methanol solution. Single crystals, albeit of very modest quality showing a severe disorder of the other complex in the asymmetric unit, were also obtained for the 1 : 1 complex of **2** with quinuclidine **7** upon slow evaporation from chloroform. The X-ray crystallographic analysis shows that compound **2** forms a dimeric structure, in which one of the oxygen atoms of each salophen unit forms a bridge between two Zn centres. The structure of the dimer is shown in Fig. 1 and relevant bond distances and angles are listed in Table 1. The two salophen units do not show the antiparallel orientation found in the structures reported by Singer and Atwood[5] and by Reek and co-workers.[12] The two different N–arene torsion angles in the salophen backbone cause a slight geometric asymmetry that makes each Zn atom a chiral centre and, consequently, each dimer a diastereomer in which both Zn centres were found to have the same chirality. The space group is centrosymmetric and both enantiomeric dimers are present in the crystal. The isolation of such a complex demonstrates that isopropyl groups in the 3,3′ positions do not prevent the formation of dimeric structures, at least in the solid state.

Unlike the free receptor **2**, its 1 : 1 complex with quinuclidine is monomeric, as shown in Fig. 2. Relevant bond distances and angles are reported in Table 1. The molecular structure of this complex features the Zn centre in a five-coordinated square pyramidal geometry in which quinuclidine occupies the apical position. The zinc atom is 0.43 Å above the mean plane of the N_2O_2 coordination, a distance close to the value of 0.40 Å reported by Atwood for the complex of zinc 3,3′,5,5′-tetra-*tert*-butylsalophen with pyridine[5] and to the value of 0.41 Å recently reported by Lin and co-workers[14] for a pyridine adduct of a similar complex in which the *o*-phenylenediamine moiety is replaced by 2,3-diaminopyridine. Also the Zn–N distance of 2.10(1) Å in **2**·**7** compares well with the corresponding distances of 2.103(2) and 2.127(2) Å, respectively, reported for the above pyridine complexes.[5,14] The salophen ligand appears to be severely bent. The distance between the atoms surrounding the metal centre and the α-methylene groups of quinuclidine corresponds to the sum of van der Waals radii, clearly suggesting that the convex shape of the salophen backbone is a consequence of the steric compression exerted by the quinuclidine ligand.[15]

Table 1 Selected bond lengths (Å) and angles (°) for **2**·**2** and **2**·**7**

2·**2**

Zn(1A)–O(1A)	2.044(3)	Zn(1A)–O(1B)	2.069(3)
Zn(1A)–N(8A)	2.108(3)	Zn(1A)–N(19A)	2.088(3)
Zn(1A)–O(26A)	1.955(3)	Zn(1B)–O(1A)	2.072(3)
Zn(1B)–O(1B)	2.065(3)	Zn(1B)–N(8B)	2.106(3)
Zn(1B)–N(19B)	2.113(3)	Zn(1B)–O(26B)	1.934(3)
O(1A)–Zn(1A)–O(1B)	84.01(11)	O(1A)–Zn(1A)–O(26A)	100.70(11)
O(1B)–Zn(1A)–O(26A)	112.65(11)	N(8A)–Zn(1A)–N(19A)	77.79(13)
O(1A)–Zn(1B)–O(1B)	83.40(11)	O(1A)–Zn(1B)–O(26B)	114.52(12)
O(1B)–Zn(1B)–O(26B)	101.47(12)	N(8B)–Zn(1B)–N(19B)	77.81(13)

2·**7**

Zn(1)–O(26)	1.96(1)	Zn(1)–O(1)	1.97(1)
Zn(1)–N(19)	2.10(1)	Zn(1)–$N(1)_{guest}$	2.10(1)[a]
Zn(1)–N(8)	2.12(1)		
O(26)–Zn(1)–O(1)	96.6(4)	O(26)–Zn(1)–N(19)	88.5(4)
O(1)–Zn(1)–N(19)	148.8(5)	O(26)–Zn(1)–$N(1)_{guest}$	96.9(5)[a]
O(1)–Zn(1)–N(1)	100.9(5)	N(19)–Zn(1)–$N(1)_{guest}$	109.0(5)[a]
O(26)–Zn(1)–N(8)	158.2(5)	O(1)–Zn(1)–N(8)	88.0(4)
N(19)–Zn(1)–N(8)	77.0(4)	$N(1)_{guest}$–Zn(1)–N(8)	103.1(5)[a]

[a] $N(1)_{guest}$ is the quinuclidine nitrogen.

Optical properties and binding studies

Absorption and emission spectra of compound **1–3** are reported in Fig. 3 and the relevant photophysical data are summarized in Table 2. Complexes **1** and **2** show broad, unstructured absorption bands in the 300–500 nm region and fluorescence bands (λ_{ex} = 350 nm) are centered in the

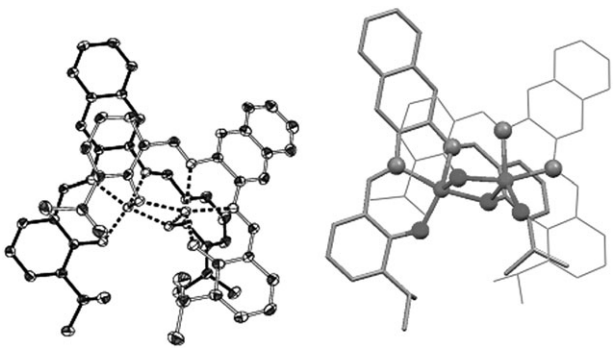

Fig. 1 (Left) Ellipsoid plot of the crystallographically independent dimer in structure **2**·**2** (ellipsoids are drawn at the 30% probability level, hydrogens are omitted for clarity). (Right) Sticks/wireframe/ball and sticks representation of the dimer. The methanol molecule is omitted for clarity.

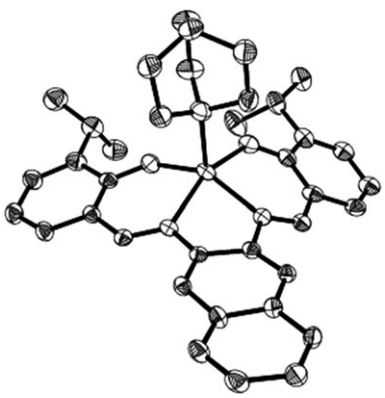

Fig. 2 A view of the **2**·**7** complex with thermal ellipsoids at 30% level. The hydrogen atoms and the solvent chloroform are omitted for clarity. Only the non-disordered complex of the two complexes in the asymmetric unit is shown.

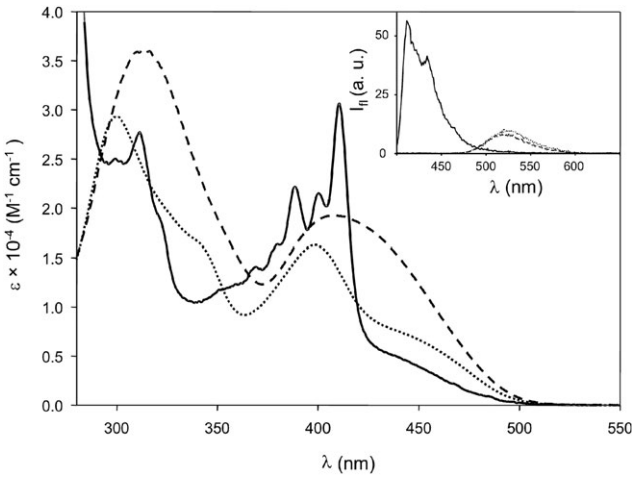

Fig. 3 Absorption and fluorescence (λ_{ex} = 350 nm) spectra of zinc–salophen compounds **1** (···), **2** (--), and **3** (—) in air-equilibrated $CHCl_3$ at room temperature.

500–550 nm region. Complex **3** shows a rather different behavior in that its absorption spectrum presents structured bands in the 350–470 nm and the emission (λ_{ex} = 350 nm) falls in the 400–500 nm region.

Typical Lambert–Beer plots are shown in Fig. 4. Strictly speaking, the good linearity of such plots does not rule out the possibility that the actual structure of complexes in solution is that of strong dimers which do not dissociate appreciably into monomer even in the very dilute solutions used for optical measurements. However, we rather believe that the close adherence of optical data to the Lambert–Beer law at different wavelengths provides a strong indication of the lack of any significant dimerization under the given conditions.

The binding of amines **4–7** to zinc–salophen compounds **1–3** was investigated by standard absorption titrations. Addition of increasing amounts of amine to a given zinc–salophen compound in air equilibrated chloroform at 25 °C caused reproducible absorbance changes in 350–500 nm region, where absorption of the added amine is negligible. During titration, the spectra of **1** and **2** showed a gradual increase of absorbance along with a red shift of the band in the 400–450 nm region, whereas the absorbance of **3** decreased with no substantial shift of the absorption band.

A typical titration experiment is shown in Fig. 5. Absorbance values at a fixed wavelength were fitted to the binding isotherm for 1 : 1 complexation (eqn (1)), where [S] is the analytical concentration of added substrate, A is the corresponding absorbance, $[R]_o$ and A_o are the concentration and the absorbance, respectively, of the receptor prior to the addition of the substrate, and ΔA_∞ is equal to $A_\infty - A_o$, where A_∞ refers to the substrate–receptor complex.

$$A = A_0 + \Delta A_\infty \frac{[R]_0 + K^{-1} + [S] - \sqrt{([R]_0 + K^{-1} + [S])^2 - 4[S][R]_0}}{2[R]_0} \quad (1)$$

Table 2 Absorption and luminescence data for zinc–salophen compounds **1**, **2**, and **3** in air-equilibrated $CHCl_3$ solution at room temperature

	Absorption, λ_{max}/nm	ε_{max}/L mol^{-1} cm^{-1}	Fluorescence, λ_{max}/nm
1	299	29 300	526
	398	16 200	
2	314	36 100	516
	408	19 200	
3	311	27 700	411
	409	30 100	

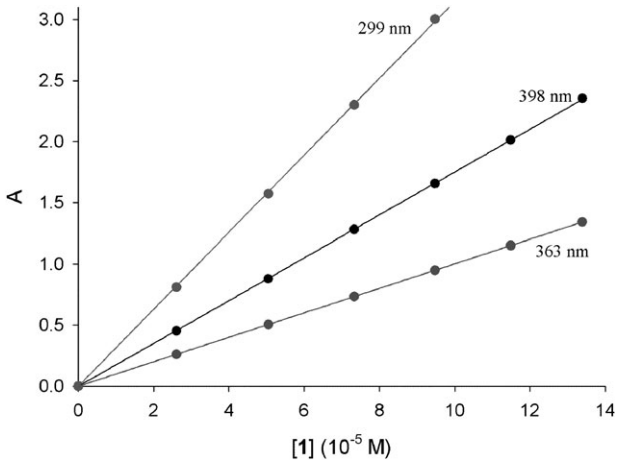

Fig. 4 Absorbance *vs.* concentration plots for compound **1** showing close adherence to the Lambert–Beer law.

The presence of well defined isosbestic points, as well as the close adherence of titration data to the binding isotherm of eqn (1) indicates that absorbance changes are attributable to a 1 : 1 association phenomenon, in line with the stoichiometry observed in the solid state, and strongly corroborates the idea that compounds **1–3** are monomeric under the conditions of the titration experiments. Emission titrations under the same conditions used for absorption titrations were carried out in

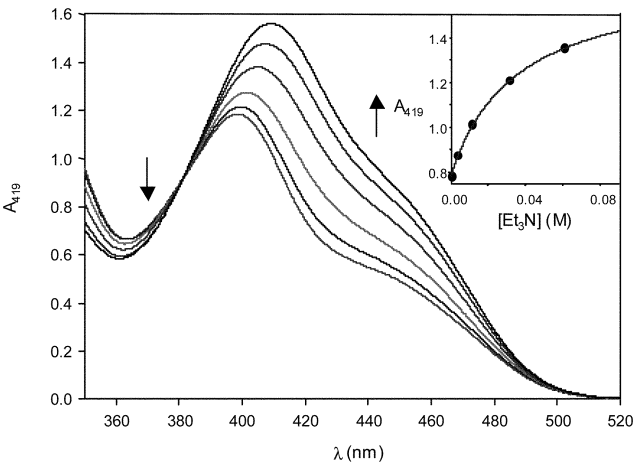

Fig. 5 Absorption spectra of **1** upon titration of a 7.7 × 10^{-5} M solution with triethylamine in $CHCl_3$ at room temperature. The inset shows the titration plot obtained at 419 nm; the full line is the fitted curve relative to the formation of a 1 : 1 complex, K = 28 M^{-1}.

Table 3 Association constants (K/M^{-1} in $CHCl_3$ at 298 K) for complexes between zinc–salophen compounds **1–3** with amines **4–7**[a]

	1	2	3
Diisopropylethylamine	<2	<2	48.9 ± 0.6
Triethylamine	28 ± 3	54 ± 14 (54 ± 8)[b]	5500 ± 900 (5500 ± 700)[b]
Dimethylethylamine	1500 ± 300 (1600 ± 400)[b]	1900 ± 400 (1800 ± 300)[b]	97 000 ± 15 000
Quinuclidine	$>10^6$	$>10^6$	$>10^6$

[a] From UV-Vis titrations, unless otherwise stated. Errors are calculated as $\pm 2\sigma$. [b] From luminescence titrations (λ_{exc} = 350 nm).

selected cases. Binding constants evaluated according to the two methods were in good agreement with each other.

Binding data (Table 3) show that complexation of amines **4–7** to zinc–salophen complexes **1–3** is strongly dependent on amine structure. Comparison with the pK_a[16] indicates that amine basicity plays a very minor role in complexation. Diisopropylethylamine, which is the most basic and the bulkiest substrate in the lot, shows the lowest binding affinity. With quinuclidine, in which the steric hindrance around the nitrogen is at a minimum, all binding constants are so large that only a lower limit of 10^6 M^{-1} could be estimated. It appears therefore that the amine complexation with the zinc–salophen receptors is largely dominated by steric effects. In other words, the binding affinity is controlled by the steric compression exerted by the incoming amine ligand on the receptor backbone, which is clearly revealed by the bent salophen moiety in the molecular structure of the **2**·**7** complex (Fig. 2).

The dominance of steric effects on amine binding offers a possible explanation for the highest binding affinities shown by receptor **3** compared with **1** and **2**. Molecular models show that the phenanthrene-based salophen can adopt a U-shaped bent geometry to avoid repulsive interactions between the imine hydrogens and the nearest phenanthrene hydrogens (Fig. 6).[17] It is readily seen that the U-shaped structure resembles closely the bent geometry assumed by compound **2** in the X-ray crystal structure in Fig. 2. It is therefore very likely that **3** displays the highest binding affinities because it has to pay a reduced energy cost upon amine binding.

At first, the remarkable selectivity observed in the binding of zinc–salophen receptors to tertiary amines caused much surprise. Although the stability order **7** > **6** > **5** > **4** was quite predictable, the magnitude, and even more so, the spread of binding affinity was unexpected. A major reason for this is the scarcity of binding data on analogous systems for useful comparison. To the best of our knowledge, the only quantitative data on binding between zinc and tertiary amines available in the literature refer to the association of zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP) with triethylamine ($\log K$ = 1.1) and DABCO ($\log K$ = 5.2) in benzene at 25 °C.[18] These figures translate into a K value of 13 M^{-1} for triethylamine and one of 8×10^4 M^{-1} for quinuclidine, the latter being an admittedly rough estimate based on the assumption that the only difference between DABCO and quinuclidine is a statistical factor 2 in favor of the former. Taking into account that the ZnTPP binds to pyridine in benzene about 6 times more strongly than in chloroform due to solvation of pyridine by hydrogen bonding,[19] comparison of binding constants of triethylamine and quinuclidine to ZnTPP with those of Table 3 shows that zinc–salophen receptors **1–3** are more effective and selective binders than ZnTPP.

Fig. 6 Computer generated ball-and-stick picture of the zinc–salophen complex **3**.

Conclusions

In the present paper we have shown that binding of zinc–salophen compounds to tertiary amines is subjected to a dramatic influence of steric effects that leads to an unprecedented selectivity among the series of amines here investigated. The very finding that axial coordination of tertiary amines is stronger for zinc–salophen compounds than for zinc–porphyrins offers prospect for their use in the construction of more stable supramolecular assemblies based on ligand–metal coordination.[7,20]

Experimental

The best commercially available chemicals were obtained and used without further purification unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with either a 200 MHz or a 300 MHz spectrometer. Diisopropylethylamine **4**, triethylamine **5**, and dimethylethylamine **6** were distilled over sodium before use. 3-Isopropylsalicylaldehyde was available from a previous work.[21] Spectrophotometric grade chloroform and chloroform-d_1 were used as received.

General procedure for the synthesis of compounds 1–3

A solution of 3-isopropylsalicylaldehyde (0.104 g, 0.632 mmol), the appropriate 1,2-diaminoarene (0.316 mmol), and $Zn(OAc)_2 \cdot 2H_2O$ (0.069 g, 0.316 mmol) in MeOH (2.5 mL) was refluxed for 1 h. The mixture was cooled to room temperature and filtered. The final products were obtained as yellow solids.

Zinc–salophen complex 1. was prepared from 3-isopropylsalicylaldehyde and 1,2-diaminobenzene. The desired product was obtained in 95% yield. Mp 334–336 °C. Elemental analysis: calc. (%) for $C_{26}H_{26}N_2O_2Zn$: C, 67.32; H, 5.65; N, 6.04; found: C, 67.00; H, 5.82; N, 6.03. ^1H NMR (300 MHz, acetone-d_6) δ 8.47 (s, 2H); 7.33–7.26 (m, 4H); 7.15–7.12 (dd, 2H); 6.97–6.94 (d, 2H); 6.53–6.47 (t, 2H); 3.48 (m, 2H); 1.11 (s, 12H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 208.7, 133.0, 131.7, 129.2, 128.9, 126.8, 126.6, 123.1, 121.6, 121.3, 32.6, 23.4 ppm. HRMS-ESI-TOF for $C_{26}H_{26}N_2O_2ZnNa^+$ calc.: 485.1183; found: 485.1172.

Table 4 Crystal data and parameters for **2**·**2** and **2**·**7**

Structure	**2**·**2**	**2**·**7**
Formula	$C_{60}H_{56}N_4O_4Zn_2 \cdot CH_3OH$	$C_{30}H_{28}N_2O_2\,Zn \cdot NC_7H_{13} \cdot CHCl_3$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
M_r	1059.91	718.25
a/Å	13.409(3)	21.550(4)
b/Å	14.202(3)	11.749(2)
c/Å	15.345(3)	30.535(1)
α/°	109.09(3)	90
β/°	99.73(3)	109.83(3)
γ/°	99.82(3)	90
V/Å^3	2640(1)	7273(2)
Z	2	8
D_c/g cm^{-3}	1.334	1.312
Crystal size/mm	0.40 × 0.20 × 0.15	0.20 × 0.04 × 0.04
μ/mm^{-1}	0.962	0.883
Completeness	94.5% (θ = 27.3°)	97.4% (θ = 22.5°)
R_{int}	0.071	0.121
R^a	0.065	0.195
Data/restraints/parameters	11 252/0/654	9272/2976 /1339
GOOF	1.032	1.124

^{a} $F^2 > 2\sigma(I)$.

Zinc–salophen complex 2. was prepared from 3-isopropylsalicylaldehyde and 2,3-diaminonaphthalene. The desired product was obtained in 82% yield. Mp 392–395 °C. Elemental analysis: calc. (%) for $C_{30}H_{28}N_2O_2Zn \cdot 1/2H_2O$: C, 68.90; H, 5.59; N, 5.36; found: C, 68.87; H, 5.50; N, 5.37. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.76 (s, 2H); 7.94 (m, 4H); 7.53–7.50 (m, 2H); 7.16–7.14 (d, 2H); 7.00–6.97 (d, 2H); 6.48–6.43 (t, 2H) 3.52 (m, 2H); 1.17–1.14 (d, 12H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 204.9, 163.4, 141.4, 139.4, 132.7, 132.3, 129.6, 127.6, 125.9, 119.7, 114.0, 113.9, 113.2, 113.1, 26.5, 26.4, 21.6, 21.5 ppm. HRMS-ESI-TOF for $C_{30}H_{28}N_2O_2ZnNa^+$ calc.: 535.1340; found: 535.1355.

Zinc–salophen complex 3. was prepared starting from 3-isopropylsalicylaldehyde and 9,10-diaminophenanthrene. The desired product was obtained in 80% yield. Mp 380–383 °C. NMR spectra could not be recorded due to extremely low solubility in all deuterated solvents. Elemental analysis: calc. (%) for $C_{34}H_{30}N_2O_2Zn \cdot 1/2H_2O$: C, 71.27; H, 5.45; N, 4.89; found: C, 71.52; H, 5.31; N, 4.63. FAB-MS (NBA) m/z 500.2 [$C_{34}H_{32}N_2O_2$].

X-Ray crystal structure determinations

Single crystals of the analyzed compounds were selected and mounted on a cryo-loop for single-crystal X-ray data collection on a BRUKER-NONIUS KAPPACCD diffractometer, geared with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and provided of an APEXII area detector and an OXFORD CRYOSTREAM cryogenic device (data collected at 173 K). Structure solution was performed by SHELXS-97,[22] with subsequent refinement on F^2 by full-matrix least squares (SHELXL-97). Hydrogen atoms were calculated to their idealized positions and refined with a riding model (isotropic displacement parameters 1.2 or 1.5 times C anisotropic displacement parameters). Multiscan absorption correction was applied to the data (SADABS). The complex **2**·**7** crystallised as extremely thin needles with two complexes in an asymmetric unit. Only one of the crystallographically independent complex is not disordered, rest of the structure being severely disordered resulting a very high R-value. The other complex shows extensive 180° rotational disorder coupled with disordered solvent chloroform molecule and thus *ca.* 2970 restraints had to be imposed to the model in the final refinements in order to prevent chemically unreasonable geometrical parameters. Crystallographic details are presented in Table 4.

CCDC reference numbers 618843 and 618844.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700723j

Absorption and luminescence spectra and titrations

Absorption and luminescence spectra were recorded at 25 °C in air-equilibrated $CHCl_3$ solutions in the concentration range of 6×10^{-6}–7×10^{-5} M.

Titrations were carried out at 25 °C in air-equilibrated $CHCl_3$ by adding increasing amounts of the amine to a solution of the zinc–salophen complex and by following variations of absorbance and/or luminescence at fixed wavelengths. Titration data were fitted to the standard binding isotherm for 1 : 1 complexation of eqn (1) after taking into account the dilution of the solution during the titration. In the case of luminescence titrations, emission spectra were recorded upon excitation at 350 nm and fluorescence intensity values detected throughout the experiments were corrected for the nonlinear intensity *vs.* absorbance response of the instrument.[23] Upon addition of increasing amounts of amine, the intensity of the emission bands of **2** increased, while that of **1** and **3** decreased.

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References

1 M. A. Medina, J. L. Urdiales, C. Rodríguez-Caso, F. J. Ramírez and F. Sánchez-Jiménez, *Crit. Rev. Biochem. Mol.*, 2003, **38**, 23–59.
2 (*a*) T. Iyobe, T. Asada, K. Kawata and K. Oikawa, *J. Health Sci.*, 2004, **50**, 148–153; (*b*) A. Mirmohseni and A. Oladegaragoze, *Sens. Actuators, B: Chem.*, 2003, **89**, 164–172; (*c*) F. W. Fifield and P. J. Haines, in *Enviromental Analytical Chemistry*, Blackwell, London, 2nd edn, 2000, p. 499; (*d*) Y. Ono, I. Somiya and Y. Oda, *Water Res.*, 2000, **34**, 890–894; (*e*) M. Abalos, J. M. Bayona and F. Ventura, *Anal. Chem.*, 1999, **71**, 3531–3537; (*f*) S. Fuselli, S. Cerquiglini and E. Chiacchierini, *Chim. Ind.*, 1978, **60**, 711–718.
3 (*a*) G. W. Gokel, W. M. Leevy and M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723–2750; (*b*) T. Hayashi, M. Nonogushi, T. Aya and H. Ogoshi, *Tetrahedron Lett.*, 1997, **38**, 1603–1606.
4 (*a*) G. Lu, J. E. Grossman and J. B. Lambert, *J. Org. Chem.*, 2006, **71**, 1769–1776; (*b*) E. K. Feuster and T. E. Glass, *J. Am. Chem. Soc.*, 2003, **125**, 16174–16175; (*c*) F. Sancenón, R. Martinez-Manez, M. A. Miranda, M. J. Seguí and J. Soto, *Angew. Chem., Int. Ed.*, 2003, **42**, 647–650; (*d*) E. Mertz and S. C. Zimmermann, *J. Am. Chem. Soc.*, 2003, **125**, 3424–3425; (*e*) V. S.-Y. Lin, C.-Y. Lai,

J. Huang, S.-A. Song and S. Xu, *J. Am. Chem. Soc.*, 2001, **123**, 11510–11511; (*f*) G. J. Mohr, N. Tirelli, C. Lohse and U. E. Spichiger-Keller, *Adv. Mater.*, 1998, **10**, 1353–1357.
5 A. L. Singer and D. A. Atwood, *Inorg. Chim. Acta*, 1998, **277**, 157–162.
6 (*a*) F. Gao, W.-J. Ruan, J.-M. Chen, Y.-H. Zhang and Z.-A. Zhu, *Spectrochim. Acta, Part A*, 2005, **62**, 886–895, and references therein; (*b*) A. W. Kleij, M. Kuil, D. M. Tooke, M. Lutz, A. L. Spek and J. N. H. Reek, *Chem.–Eur. J.*, 2005, **11**, 4743–4750; (*c*) G. A. Morris, H. Zhou, C. L. Stern and S. T. Nguyen, *Inorg. Chem.*, 2001, **40**, 3222–3227.
7 A. W. Kleij, M. Kuil, D. M. Tooke, M. Lutz, A. L. Spek and J. N. H. Reek, *Chem.–Eur. J.*, 2005, **11**, 4743–4750.
8 (*a*) Y.-M. Shen, W.-L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 1559–1562; (*b*) T. Katsuki, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, Wiley-VHC, New York, 2nd edn, 2000, ch. 6B, pp. 287–325; (*c*) E. N. Jacobsen and M. H. Wu, in *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, New York, 1999, ch. 18.2, pp. 649–677.
9 (*a*) A. Dalla Cort, L. Mandolini, C. Pasquini and L. Schiaffino, *Org. Biomol. Chem.*, 2006, **4**, 4543–4546; (*b*) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.-I. Noro and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2684–2687; (*c*) S.-S. Sun, C. Stern, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 6314–6326; (*d*) K. E. Splan, A. M. Massari, G. A. Morris, S.-S. Sun, E. Reina, S. T. Nguyen and J. T. Hupp, *Eur. J. Inorg. Chem.*, 2003, 2348–2351; (*e*) K. Chichak, U. Jacquemard and N. R. Branda, *Eur. J. Inorg. Chem.*, 2002, 357–368; (*f*) W. Huang, S. Gou, D. Hu, S. Chantrapromma, H.-K. Fun and Q. Meng, *Inorg. Chem.*, 2002, **41**, 864–868.
10 (*a*) M. La Deda, M. Ghedini, I. Aiello and A. Grisolia, *Chem. Lett.*, 2004, **33**, 1060–1061; (*b*) P. G. Cozzi, L. S. Dolci, A. Garelli, M. Montalti, L. Prodi and N. Zaccheroni, *New J. Chem.*, 2003, 692–697; (*c*) K. E. Splan, A. M. Massari, G. A. Morris, S.-S. Sun, E. Reina, S. T. Nguyen and J. T. Hupp, *Eur. J. Inorg. Chem.*, 2003, 2348–2351.
11 C. Tsz Lui Ma and M. J. MacLachlan, *Angew. Chem., Int. Ed.*, 2005, **44**, 4178–4182.
12 A. W. Kleij, M. Kuil, M. Luts, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. Van Leeuwen and J. N. H. Reek, *Inorg. Chim. Acta*, 2006, **359**, 1807–1814.
13 A. W. Kleij, D. M. Tooke, A. L. Spek and J. N. H. Reek, *Eur. J. Inorg. Chem.*, 2005, 4626–4634.
14 K.-H. Chang, C.-C. Huang, Y.-H. Liu, Y.-H. Hu, P.-T. Chou and Y.-C. Lin, *Dalton Trans.*, 2004, 1731–1738.
15 Comparison with the analogous complexes between zinc–salophen compounds and pyridine or methanol described in ref. 11 shows that in these cases the salophen ligand is much less bent.
16 pK_a values in water at 25 °C are 10.16 for dimethylethylamine, 10.75 for triethylamine, and 10.95 for quinuclidine (data from *IUPAC Dissociation Constant of Organic Bases in Aqueous Solution*, Butterworths, London, 1965). The pK_a value of diisopropylethylamine is 11.44 (T. Fujii, H. Nishida, Y. Abiru, M. Yamamoto and M. Kise, *Chem. Pharm. Bull.*, 1995, **43**, 1872–1877).
17 The alternative N-shaped structure with the imine bonds on different sides of the plane shows to be unfeasible since simultaneous interaction of the four donor atoms with the metal centre would be impossible.
18 N. Sakuragi, K. Ichimura and H. Sakuragi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1944–1949.
19 S. J. Cole, G. C. Curthoys, E. A. Magnusson and J. N. Phillips, *Inorg. Chem.*, 1972, **11**, 1024–1028.
20 G. Ercolani, *Struct. Bonding (Berlin)*, 2006, **121**, 167–215.
21 A. Dalla Cort, L. Mandolini, G. Palmieri, C. Pasquini and L. Schiaffino, *Chem. Commun.*, 2003, 2178–2179.
22 G. M. Sheldrick, *SHELXTL*, Madison, WI, USA, 2001.
23 A. Credi and L. Prodi, *Spectrochim. Acta, Part A*, 1998, **54**, 159–170.

