DOI: 10.1002/chem.200500704

Tunable N-substitution in Zwitterionic Benzoquinonemonoimine Derivatives: Metal Coordination, Tandemlike Synthesis of Zwitterionic Metal Complexes, and Supramolecular Structures

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Dedicated to Professor D. M. P. Mingos

Abstract: Full details on a very efficient transamination reaction for the synthesis of zwitterionic *N,N′*-dialkyl-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium derivatives $[C_6H_2(=NHR)_2(=O)_2]$ **5**–**16** are reported. The molecular structures of zwitterions **5** (R = CH_3) in **5**·H_2O, **13** (R = CH_2CH_2OMe), **15** (R = $CH_2CH_2NMe_2$), and of the parent, unsubstituted system $[C_6H_2(=NH_2)_2(=O)_2]$ **4** in **4**·H_2O have been established by single-crystal X-ray diffraction. This one-pot preparation can be carried out in water, MeOH, or EtOH and allows access to new zwitterions with N-substituents bearing functionalities such as −OMe (**13**), −OH (**9**–**12**), $-NR^1R^2$ with $R^1 = \text{ or } \neq R^2$ (**14**–**16**) or an alkene (**8**), leading to a rich coordination chemistry and allowing fine-tuning of the supramolecular arrangements in the solid state. As previously described for **15**, which reacted with $Zn(acac)_2$ to afford the octahedral Zn^{II} complex $[Zn\{C_6H_2(=NCH_2CH_2NMe_2)O(=O)(NHCH_2CH_2NMe_2)\}_2]$ (**20**), ligands **13** and **16** with coordinating "arms" afforded with $Zn(acac)_2$ the 2:1 adducts $[Zn\{C_6H_2(=NCH_2CH_2X)O(=O)(NHCH_2CH_2NX)\}_2]$ **19** (X = OMe) and **21** (X = NHEt), with N_2O_4 and N_4O_2 donor sets around the octahedral Zn^{II} center, respectively. Furthermore, zwitterions **15** and **16** reacted with $ZnCl_2$ to give the stable, crystallographically characterized Zn^{II} zwitterionic complexes $[ZnCl_2\{C_6H_2(=NCH_2CH_2NR^1R^2)O(=O)(NHCH_2CH_2NHR^1R^2)\}]$ **22** ($R^1 = R^2 =$ Me) and **23** (R^1 = Et, R^2 = H) by means of an unprecedented, tandemlike synthesis in which 1) the two pendant amino groups of the organic benzoquinonemonoimine zwitterionic precursor favor metal coordination and proton transfer and 2) the saturated linker prevents π-conjugation between the charges. The nature of the structural arrangements in the solid state for both inorganic (**20**, **22**, **23**) and organic (**5**, **9**, **13**, and **15**) molecules is determined by subtle variations in the nature of the N-substituent on the zwitterion precursor.

Keywords: coordination modes · organic synthesis · quinones · supramolecular chemistry · zwitterions

Introduction

Noncovalent interactions play a key role in the fields of chemistry, molecular biology, and material science.[1] Numerous supramolecular chemical assemblies have been obtained by carefully selecting building blocks made of organic ligands containing appropriate functional groups.[2] Considering the importance of noncovalent interactions in nature and the large number of natural quinonoid compounds available, it appears that studying the supramolecular properties of quinonoid molecules should provide an interesting field of research.[3] Among the natural quinones that contain an acidic proton, some play an important role as bioinhibitors,[4] because they can interact with the ATP binding site through hydrogen bonding.[4j]

Recently, zwitterionic N-substituted benzoquinonemonoimine derivatives (**2**) were shown to result from proton migration from the oxygen of a postulated hydroxyquinone intermediate **1** onto the more basic nitrogen site [Eq. (1)].[5] The first member of this new class of quinones (R = *t*Bu)[5] has attracted considerable theoretical interest, as it is a rare

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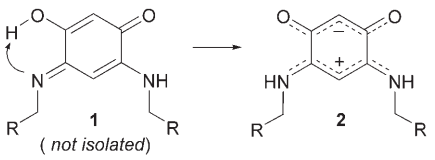
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Supporting information for this article contains a description of the molecular packing in **4**·H_2O and **5**·H_2O



(1)

example of a potentially antiaromatic zwitterion being more stable than its canonical forms.[6]

Such quinonoids display interesting supramolecular structural properties,[5,6a,7] and appear very attractive in organic chemistry,[6a,7] color chemistry,[8] and coordination chemistry[6a,9] owing to their remarkable chemical and physical properties: 1) as zwitterions they are strongly dipolar (electrostatic interactions), 2) they possess two hydrogen-donor sites and two hydrogen-acceptor sites (hydrogen-bonding interactions), 3) they have a conjugated π system (π–π interaction), and 4) it is possible to vary the nature of the N-substituent (tuning of the steric properties and introduction of heteroatoms and/or hydrogen-donor and -acceptor sites).

However, the preparation of a wide range of such NCH_2R-substituted zwitterions could not be achieved by the initial synthetic procedure owing to the need to use highly reactive acid chlorides,[5,6a] in which the choice of other functional groups is limited. For further applications of this class of molecules, in particular as colorants, a "greener" synthesis (i.e. without organic solvent) was of great interest.

A new, efficient synthesis of various functional N-substituted, 6π+6π-electron zwitterionic benzoquinonemonoimine derivatives involves the first transamination reactions in quinonoid chemistry.[10] This one-pot preparation can often be performed in water and provides an access to new zwitterions not available by the previously reported methods.[5,6a] It allows a fine-tuning of the solubility of these molecules, which is a key point for their subsequent applications. Furthermore, the introduction of various functionalities on the zwitterionic skeleton opens new possibilities in supramolecular chemistry and for the synthesis of novel coordination complexes.

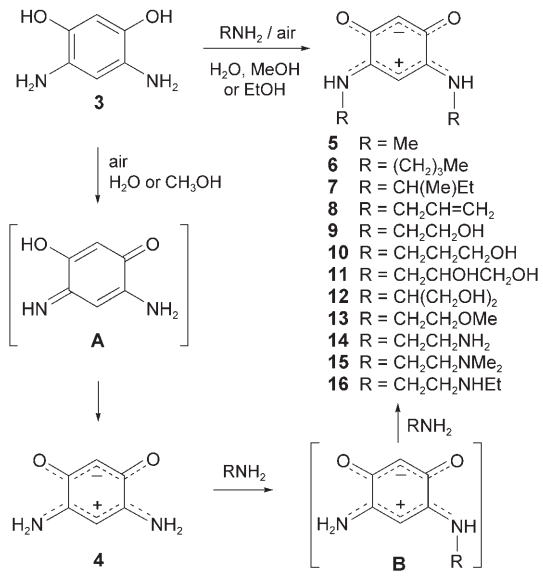
Among them, zwitterionic metal complexes have been recognized as an important class of molecules endowed with interesting structural, electronic, magnetic, nonlinear optical, or catalytic properties.[11] It is usually the metal center that carries the positive charge. The reverse situation in which an integral negative charge would be formally localized on the metal center is uncommon, although this is the case, for example, in complexes derived from phosphonium ylids.[12] When the negative charge is delocalized between the metal center and the coordinated ligand through a conjugated π system, different nonzwitterionic Lewis structures can be envisaged.[12] Therefore, true zwitterionic metalates with the opposite charges separated by sp^3 carbon atoms are particularly interesting, but much less common.[11f,13] They are attracting increasing interest owing to their potential in nonlinear optics, molecular electronics, and catalysis.[12,14] In addition, the nature and geometry of the coordination sphere of Zn^{II} complexes in the presence of multifunctional ligands are of increasing relevance in bioinorganic chemistry.[15]

The formation of metal complexes from zwitterionic ligands is often limited by the low reactivity of the latter,[6a,9,16] the poor stability of the complexes,[17] or by restrictions to certain pH ranges.[16,17] We are aware of only one study reporting the preparation of a zwitterionic complex from an organic zwitterion.[11f] Its formation was, however, unexpected and not fully understood.

Herein, we wish to describe the synthesis of a range of zwitterionic quinones, their metal coordination, and supramolecular organizations. The synthesis of new ammonium metalate zwitterionic complexes from such quinonemonoimine 6π+6π organic zwitterions involves a controlled metalation operating in a tandemlike manner, with each of the initially identical pendant amino functions of the organic precursor playing a different role with anchimeric assistance. The nature of the structural arrangements in the solid state for both inorganic and organic molecules is determined by subtle variations in the nature of the N-substituent on the zwitterion precursor.

Results and Discussion

Ligand synthesis: We have extended the family of zwitterionic quinones **2** by applying our recent transamination procedure.[10a] Compound **3**·2HCl reacted smoothly at room temperature and in air with a large excess of primary amines RNH_2 in water, MeOH, or EtOH to afford the corresponding zwitterions $[C_6H_2(=NHR)_2(=O)_2]$ **5–16** in high yield (see Experimental Section; Scheme 1). The zwitterion **4** was shown to be an intermediate in this reaction.[10a] Functionalities such as OH, OMe, NR^1R^2 ($R^1 =$ or $\neq R^2$), or an alkene could thus be introduced. In contrast to **6** and **7**, which are only soluble in organic solvents, **9–12** are almost

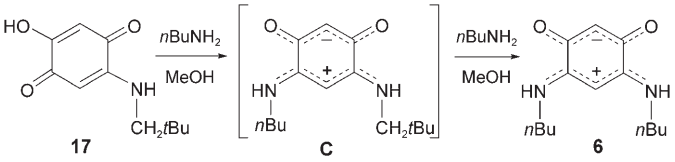


Scheme 1. One-pot synthesis of zwitterions **5–16**.

insoluble in most organic solvents, but are soluble in water owing to the presence of hydrophilic groups (-OH). Zwitterions **5** and **13**–**16** are soluble in both organic solvents and water.

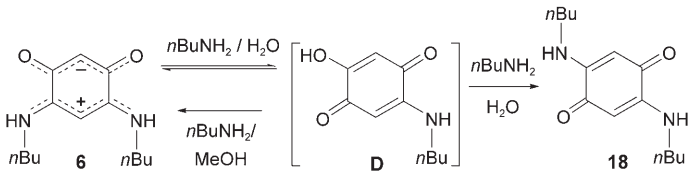
It is known that nucleophilic substitution reactions can occur smoothly on quinonoid rings. For instance, an amino group can substitute an hydroxyl group, a methoxy group, and sometimes alkyl groups of quinones.[18] However, to the best of our knowledge, substitution of an amino group by another amine was unprecedented in quinonoid chemistry (Scheme 1).[10] This transamination reaction under mild conditions may be rationalized by the fact that in the parent zwitterion **4**, the positive charge is π-delocalized between the nitrogen atoms, making the C–N carbon atoms (i.e., C3 and C5) more electrophilic. Although monosubstituted **B** would be a likely intermediate (Scheme 1), it could not be isolated owing to the fast kinetics of the reaction.

Interestingly, hydroxybenzoquinone derivatives, related to **17**,[7] react with amines to afford quinonemonoimine derivatives; this represents an important step in enzyme-catalyzed deamination reactions.[18c,d] We anticipated that reaction of **17** with *n*-butylamine could afford the unsymmetrical zwitterion **C** (Scheme 2). However, zwitterion **6** was isolated instead, showing that the amine reacted with both the carbonyl and the neopentylamino groups of **17**, probably via intermediate **C**. This constitutes the first direct synthesis of zwitterionic benzoquinonemonoimines from benzoquinones.



Scheme 2. Reaction of hydroxybenzoquinone **17** with excess amine.

Influence of the reaction time: We noticed that when **3**·2 HCl was treated with excess nBuNH$_2$ in water for a long period of time (3 days), 2,5-diaminoquinone **18** was formed in high yield. This reaction may proceed according to Scheme 3: first, the zwitterion **6** (obtained in 2 h from **3** according to Scheme 1) would be hydrolyzed under basic conditions to afford an aminohydroxyquinone intermediate **D** (see Experimental Section), as recently reported,[7] and then the OH group of **D** would be substituted by the amine in excess to afford **18**. Intermediate **D** could also react with the amine to regenerate the zwitterion **6** (Scheme 3), but the irreversible transformation **D**→**18** shifts the equilibrium between **6** and **D** to the right. In the absence of water, **6** is quantitatively obtained by the reaction of **D** with an excess of *n*-butylamine in MeOH, similarly to the reactions shown in Scheme 2.



Scheme 3. Competing reactions involving **D**.

Crystal structures of the ligands: The molecular structures of compounds **4**·H_2O, **5**·H_2O, **13**, and **15** have been elucidated by X-ray crystallography (Figure 1). A symmetry axis passes through the carbon atoms C1 and C4 of **13** and **15**. Selected bond lengths and angles are listed in Tables 1 and 2, respectively.

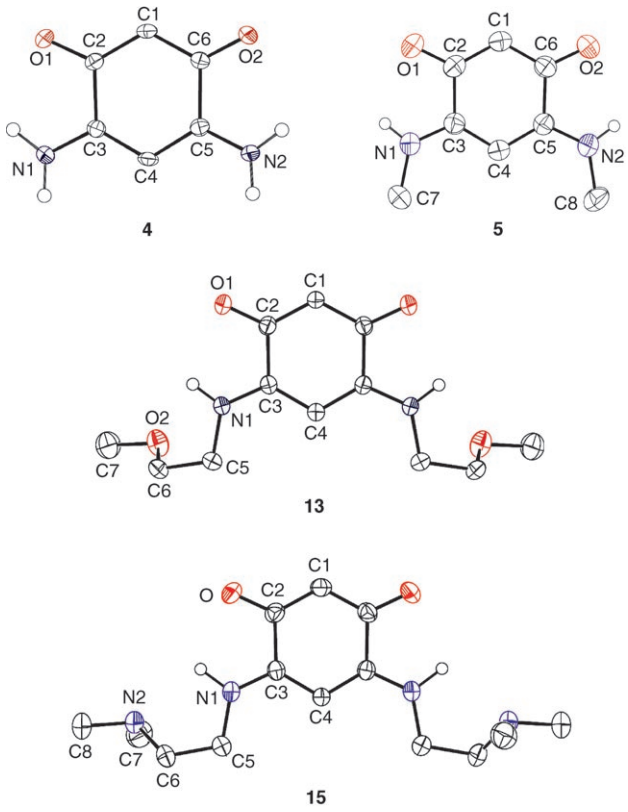


Figure 1. ORTEP views of **4** in **4**·H_2O, **5** in **5**·H_2O, **13**, and **15**. Thermal ellipsoids are drawn at the 50% probability level. Only the NH protons are shown.

Whereas more than one century ago, the air oxidation product of diaminoresorcinol was erroneously described as intermediate **A** in Scheme 1,[19] we recently concluded on the basis of ^{1}H NMR data that its true structure is **4**.[10] This has now been confirmed by an X-ray diffraction study on single crystals of **4**·H_2O, obtained by slow aerobic reaction in water of diaminoresorcinol dihydrochloride with glycin. The structure of the parent member of the family of 6π+6π-electron molecules **2** confirms its zwitterionic character, with a fully delocalized π system within the O1-C2-C1-C6-O2 and N1-C3-C4-C5-N2 moieties (Figure 1). The correspond-

Table 1. Selected bond lengths [Å] in **4**·H_2O, **5**·H_2O, **13**, and **15**.

	4·H_2O	**5**·H_2O	**13**	**15**
O1–C2	1.261(3)	1.251(2)	1.250(1)	1.252(1)
C1–C2	1.393(3)	1.387(2)	1.394(1)	1.393(1)
C1–C6	1.400(3)	1.388(2)		
C6–O2	1.251(3)	1.258(2)		
N1–C3	1.317(3)	1.310(2)	1.316(1)	1.317(1)
C3–C4	1.382(3)	1.386(2)	1.391(1)	1.383(1)
C4–C5	1.395(3)	1.383(2)		
C5–N2	1.310(3)	1.315(2)		
C2–C3	1.520(3)	1.523(2)	1.526(1)	1.527(2)
C5–C6	1.514(3)	1.526(2)		

Table 2. Selected bond angles [°] in **4**·H_2O, **5**·H_2O, **13**, and **15**.

	4·H_2O	**5**·H_2O	**13**	**15**
O1-C2-C1	126.2(2)	125.7(1)	125.8(1)	126.6(1)
O1-C2-C3	115.9(2)	116.2(2)	116.43(9)	116.1(1)
N1-C3-C4	123.7(2)	125.2(1)	124.7(1)	124.4(1)
N1-C3-C2	115.1(2)	113.7(1)	113.87(8)	113.8(1)
C2-C1-C6	122.5(2)	122.5(1)		
C3-C4-C5	119.4(2)	119.2(1)		
C2-C1-C2′			122.7(1)	123.0(1)
C3-C4-C3′			119.0(1)	118.9(1)

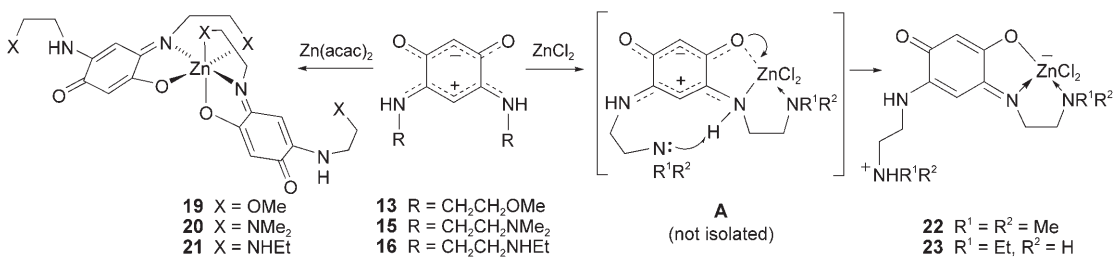
ing pairs of C=O, C=N and C=C bond lengths are very similar (Table 1). The C2–C3 and C6–C5 distances of 1.519(5) and 1.517(5) Å, respectively, correspond to single bonds and indicate a lack of conjugation between the two "6π halves" of the compound.[5,6a] As a result, molecule **4** can be considered as a trimethine oxonol subunit chemically connected to a trimethine cyanine subunit.[20] From this point of view, our transmination reaction by means of nucleophilic substitution bears similarities with reactions observed in the polymethine series.[21]

Similarly, the bond lengths found for molecules **5**·H_2O, **13**, and **15** are consistent with their zwitterionic structure, with two fully delocalized 6π subsystems that are chemically connected by two single bonds but electronically independent. In the solid state, compounds **4**·H_2O and **5**·H_2O develop intermolecular interactions with π–π stacking and strong hydrogen bonding with water molecules that generate complicated architectures (see the Supporting Information).

Coordination chemistry: The new ligands **13** and **16**, prepared similarly to **15**,[10a] show better coordination abilities toward metal precursors than **2** (R = *t*Bu) owing to the presence of additional coordinating "arms".[10a] Reactions of these ligands at room temperature with $Zn(acac)_2$ in a 2:1 ligand/metal ratio readily afforded high yields of the octahedral, neutral complexes $[Zn\{C_6H_2(=NCH_2CH_2NX)O(=O)(NHCH_2CH_2NX)\}_2]$ **19** (X = OMe), **20** (X = NMe_2),[10] and **21** (X = NHEt) which contain a uninegative, N,N,O-tridentate ligand as a result of monodeprotonation by the acac ligand (Scheme 4). No zwitterionic complex was formed.[10a] In contrast, reaction of **2** (R = *t*Bu) with $M(acac)_2$ (M = Ni, Cu, Zn) required higher temperatures and longer reaction times.[6a]

Whereas no intramolecular acid–base reaction occurs in the free ligands **15**[10a] or **16**, their reaction with $ZnCl_2$ (1 equiv) in MeOH at room temperature afforded the zwitterionic mononuclear complexes $[ZnCl_2\{C_6H_2(=NCH_2CH_2NR^1R^2)O(=O)(NHCH_2CH_2NHR^1R^2)\}]$ **22** ($R^1 = R^2 = Me$) and **23** ($R^1 = Et$, $R^2 = H$), respectively (Scheme 4). The negative charge of the metalate moiety, which is of course shared by the electronegative ligands but formally shown on the metal center in Scheme 4, is balanced by the ammonium cation resulting from intramolecular proton shift (i.e., acid–base reaction). This is consistent with the formation of intermediate **A** in which the interaction of the =NHR function with the metal center, assisted by chelation of the NR^1R^2 arm, results in an increased acidity of this =NHR proton. Whereas in earlier complexation studies[6a,9] involving **2** (R = *t*Bu),[5] prior deprotonation of the =NHR group by an external reagent was required, the amino function carried by the organic precursors **15** and **16** acts here as an intramolecular base and removes the proton, made more acidic upon coordination of the ligand to the metal. The description of complexes **22** and **23** as zwitterions is consistent with the X-ray data (Table 3 and Figure 2). In their tautomeric forms, **15** and **16** act as tridentate ligands, and the coordination sphere of the pentacoordinate metal center is completed by the two chlorine ligands.

In these Zn^{II} complexes, examination of the respective bond lengths within the O1-C2-C1-C6-O2 and N1-C3-C4-C5-N2 moieties reveal an alternation of single and double bonds, consistent with two conjugated but localized π systems (Table 3), whereas the free ligands **15** and **16** present a perfectly delocalized form. As in all previously described related crystallographic structures,[6a,9] the C2–C3 and C6–C5 distances around 1.52 Å correspond to single bonds and indicate the lack of conjugation between the two π subsystems. Interestingly, the ammonium metalates **22** and **23** are



Scheme 4. Reactions of ligands **13**, **15**, and **16** with Zn^{II} precursors.

Table 3. Selected bond lengths [Å] and angles [°] in complexes **22** and **23**.

	22	**23**
O1–C2	1.285(3)	1.268(8)
C1–C2	1.372(3)	1.379(9)
C1–C6	1.416(3)	1.395(9)
C6–O2	1.239(3)	1.240(8)
N1–C3	1.296(3)	1.287(8)
C2–C3	1.512(3)	1.521(8)
C3–C4	1.428(3)	1.430(9)
C4–C5	1.368(3)	1.344(9)
C5–N2	1.346(3)	1.358(9)
C5–C6	1.519(3)	1.523(10)
Zn–O1	2.227(2)	2.183(5)
Zn–N1	2.042(2)	2.061(5)
Zn–N3	2.246(2)	2.217(6)
Zn–Cl1	2.2815(9)	2.279(2)
Zn–Cl2	2.302(1)	2.310(2)
Cl1-Zn-Cl2	108.53(4)	112.49(8)
O1-Zn-N1	75.35(8)	75.1(2)
O2-C6-C1	125.0(2)	125.1(6)
C6-C1-C2	122.3(2)	122.5(6)
C1-C2-O1	125.1(2)	125.4(6)
N2-C5-C4	126.2(2)	125.8(7)
C5-C4-C3	119.8(2)	119.7(6)
C4-C3-N1	125.6(2)	127.3(6)

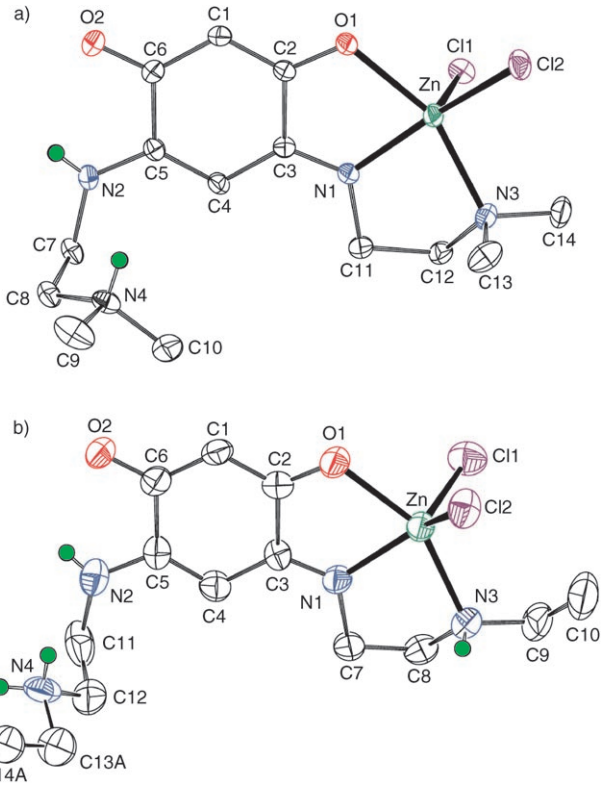


Figure 2. ORTEP views of the structure of complexes **22** (a) and **23** (b) (ellipsoids drawn at the 50% probability level).

not stabilized by intramolecular hydrogen-bonding interactions. The influence of the metal center and of the substituents R^1 and R^2 on their supramolecular structures will be discussed below.

It is worth noting that no reaction was observed between **2** (R = *t*Bu) and $ZnCl_2$ when NEt_3 was used as a base under similar conditions. This result demonstrates the assistance of the ligand pendant arm to metal coordination which induces deprotonation of the iminium nitrogen (see intermediate **A**, Scheme 4). Molecules **15** and **16** constitute rare examples of ligands operating both as a chelate and base in an anchimeric manner.

Supramolecular arrangements: A comparison of selected noncovalent interaction distances in ligands **9**,[10a] **13**, and **15**, and complexes **20**,[10a] **22**, and **23** is provided in Table 4.

Table 4. Comparison of selected noncovalent distances [Å] in ligands **9**,[10a] **13**, and **15**, and complexes **20**,[10a] **22**, and **23**.

	Intramolecular hydrogen-bonding interaction	Intermolecular hydrogen-bonding interaction	π–π interaction
9	O1···H–N1 = 2.177(3) O2···H–N2 = 2.192(3)	N1···O1 = 2.996(4) O3···O1 = 2.723(4) N2···O2 = 3.029(4) O2···O4 = 2.710(4)	C6···O2′ = 3.241(4)
13	O1···H–N1 = 2.190(3)	N1···O1 = 2.899(4)	no
15	O···H–N1 = 2.180(3) N2···H–N1 = 2.365(3)	no	C1···C4 = 3.677(4)
20	O2···H–N2 = 2.252(3) O4···H–N4 = 2.204(3)	N2···O2 = 2.962(4) N4···O1 = 2.936(4)	C15···C18 = 3.550(4)
22	O2···H–N2 = 2.191(3)	N4···O1 = 2.773(4)	C1···C4 = 3.528(4)
23	O2···H–N2 = 2.241(3)	N4···O1 = 2.718(4) N4···O2 = 2.751(4)	C1···C4 = 3.581(4)

All of them have intramolecular NH···O bonding distances in the range 2.177(3)–2.365(3) Å. Molecule **15** revealed an additional hydrogen bond owing to the presence of the basic functions $-NMe_2$ (N2···H–N1 interaction).

We have previously shown that the supramolecular network of zwitterion **2** (R = *t*Bu) forms a wavelike arrangement with head-to-tail hydrogen-bonding interactions owing to the presence of two bulky *N*-neopentyl substituents (Figure 3).[5]

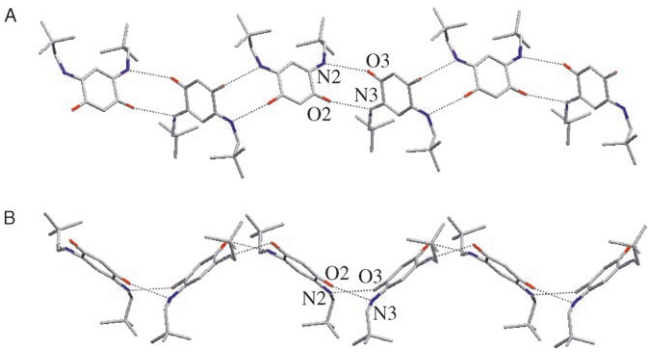


Figure 3. View of the supramolecular array generated by **2** (R = *t*Bu) in the solid state. A) Top view, and B) side view. Color coding: nitrogen, blue; oxygen, red.

Zwitterions of type **2** with no bulky N-substituents could be readily prepared by using our versatile synthetic approach. This is the case for **5**, and in contrast to the solid-state packing of **5**·H_2O (see Supporting Information), that of the solvent-free molecules consists of a head-to-tail but now almost coplanar arrangement (Figure 4), at variance to that

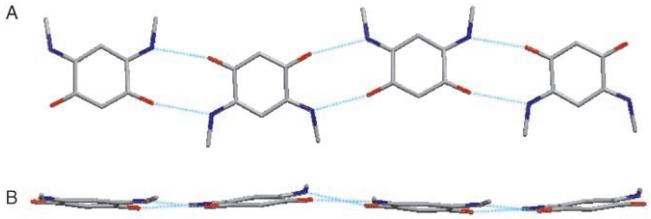


Figure 4. Views of the supramolecular array generated by **5** in the solid state. A) Top view and B) side view. Color coding: nitrogen, blue; oxygen, red.

of **2** with R = *t*Bu. This was clearly observed although the quality of the crystal did not allow a complete structural resolution (crystallization from CH_2Cl_2 with no solvent molecule incorporated in the crystal).

Although the N-substituents in **9** are bulkier than those in **5** (i.e., two $-CH_2CH_2OH$ groups), this molecule shows in the solid state a similar arrangement owing to hydrogen-bonding interactions between hydrogen donors of N1–H and O3–H and hydrogen acceptor O1 with N1···O1 and O3···O1 bond lengths of 2.996(4) and 2.723(4) Å, respectively, which force the system to become coplanar.[10] Therefore, in contrast to **2** (R = *t*Bu), molecules of **9** form a head-to-tail and coplanar 1-D supramolecular network in the solid state owing to the presence of the OH groups (i.e., two acidic protons; Figure 5).

Interestingly, the replacement of the OH proton in **9** by a methyl group (molecule **13**) prevents hydrogen-bonding interactions involving the "arms" of the ligand. As a result, these are situated out of the molecular plane, preventing formation of π–π staking (Figure 6), in contrast to **9**, which reveals a succession of layers in the solid state (see Table 4 and Figure 5B).

Although zwitterion **15** can be viewed as analogous of **2** (R = *t*Bu), this molecule leads to a different arrangement in the solid state. No intermolecular hydrogen bonding is observed owing to the presence of the hydrogen-acceptor groups $(CH_2)_2NMe_2$ that interact only through intramolecular hydrogen bonding (N1–H···N2 = 2.365(3) Å; see Figure 1 and Table 4). Thus, intermolecular interactions occur only by π–π stacking (C1···C4 = 3.677(4) Å) in a head-to-tail manner (Figure 7) instead of the head-to-tail but wavelike arrangement observed for **2** (R = *t*Bu).

The diversity of supramolecular networks generated by these ligands led us to examine the situation with the Zn^{II} complex **20**, which has two hydrogen-donor sites and several hydrogen-acceptor sites.[10a] Its crystal packing revealed intermolecular hydrogen bonding interactions in the solid

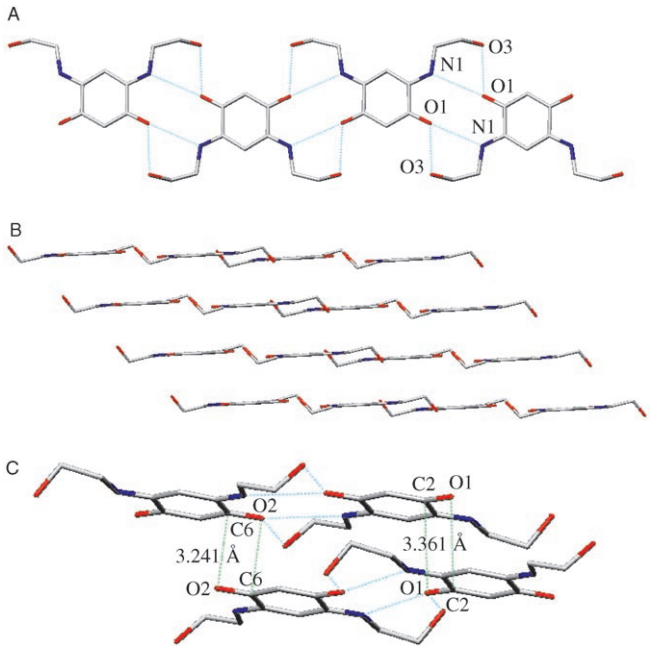


Figure 5. View of the supramolecular array generated by **9** in the solid state. A) Top view, B) side view, and C) local view of B). Color coding: nitrogen, blue; oxygen, red.

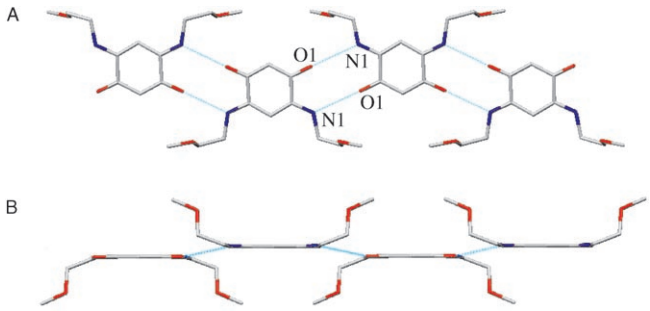


Figure 6. View of the supramolecular array generated by **13** in the solid state. A) Top view and B) side view. Color coding: nitrogen, blue; oxygen, red.

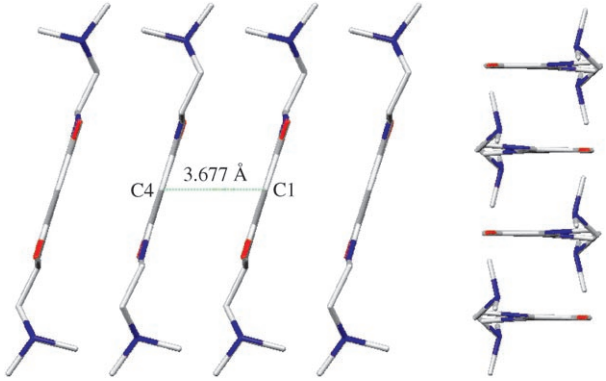


Figure 7. View of the stacking arrangement generated by **15** in the solid state. Color coding: nitrogen, blue; oxygen, red.

state with (N2···O2 = 2.962(4) and N4···O1 = 2.936(4) Å) leading to a one-dimensional wavelike chain (Figure 8). In addition, π–π interactions with a C15···C18 distance of 3.550(4) Å between two quinone rings contribute to the stability of this chain.

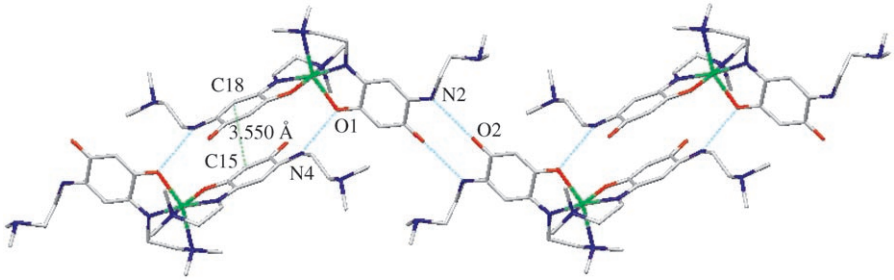


Figure 8. View of the supramolecular array generated by the Zn^{II} complex **20** in the solid state. Color coding: nitrogen, blue; oxygen, red; zinc, green.

The zwitterionic Zn^{II} complex **22** forms a pseudodimer in the solid state that is stabilized by the N4–H···O1 interaction (N4···O1 = 2.773(4) Å) and π–π stacking (see Table 3 and Figure 9).

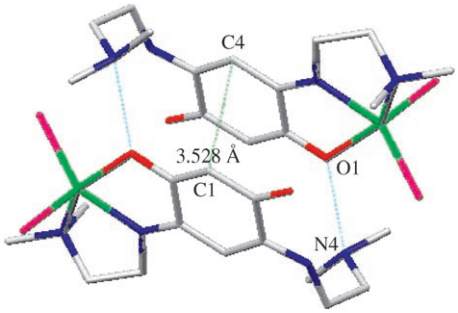


Figure 9. View of the supramolecular array generated by the zwitterionic Zn^{II} complex **22** in the solid state. Color coding: nitrogen, blue; oxygen, red; zinc, green.

Interestingly, the presence of an additional proton located on N4 in **23**, instead of the methyl group in **22**, allows further hydrogen-bonding interactions between these pseudodimers (N4···O1 = 2.718(4) and N4···O2 = 2.751(4) Å) as shown in Figure 10.

Conclusion

We have reported here full details on a new and very efficient transamination reaction for the synthesis of N-substituted zwitterionic benzoquinonemonoimine derivatives that can be carried out in water. This new one-pot synthetic approach provides access to a series of quinonoid zwitterions **5**–**16** with different N-substitutents bearing functionalities such as OMe, OH, NR^1R^2 (R^1 = or $\neq R^2$), or an alkene, leading to a rich coordination chemistry and allowing fine-tuning of the structural arrangements in the solid state. The new ligand **13** and **16** show better coordination abilities toward metal precursors than **2** (R = *t*Bu) and react with Zn(acac)$_2$, as previously shown for **15**,[10a] to afford complexes **19** and **21** with N_2O_4 and N_4O_2 donor sets around the Zn^{II} center, respectively. Zwitterions **15** and **16** were shown to react with $ZnCl_2$ to give zwitterionic complexes **22** and **23**. The nature of the arrangements in the solid state of inorganic (**20**, **22**, **23**) and organic (**5**, **9**, **13** and **15**) molecules was found to be determined by subtle variations in the nature of the N-substituent of the zwitterion precursor.

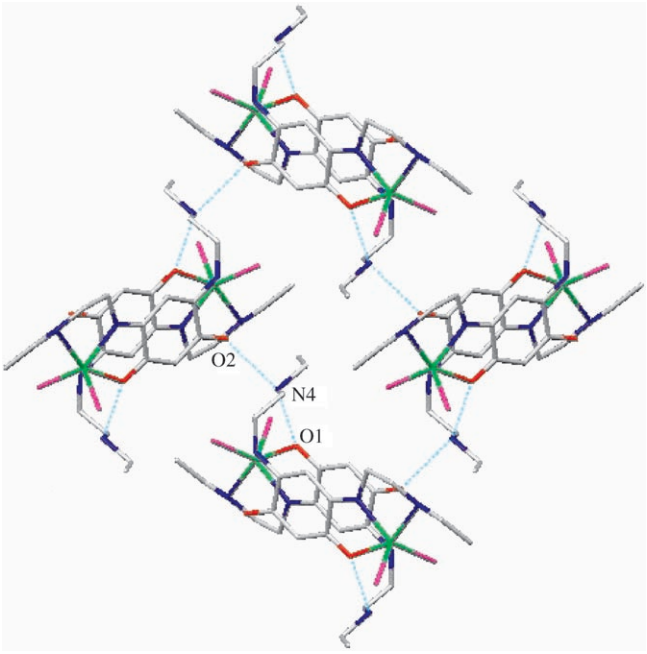


Figure 10. View of the supramolecular array generated by the zwitterionic Zn^{II} complex **23** in the solid state. Color coding: nitrogen, blue; oxygen, red; zinc, green.

Experimental Section

^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AC300 instrument. MALDI-TOF mass spectra were recorded on a Biflex III Bruker mass spectrometer. Elemental analyses were performed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". Solvents were freshly distilled under nitrogen prior to use. 4,6-Diaminoresorcinol dihydrochloride and the functional amines are commercially available. Ligands **4**–**7**, **9**, and **15**, and complex **20** were prepared according to the literature.[10a]

General procedure: Typically, diaminoresorcinol dihydrochloride (0.500 g, 2.35 mmol) was dissolved in water (ca. 10 mL) and then excess of amine (ca. 7 equiv) was added to the solution. For the compounds that

are not or only poorly soluble in water, purple crystals appeared rapidly. 30–120 minutes later, the crystals were isolated by filtration and washed with cold water, and dried in air. In other cases, details are given below.

Ligand 8: The amine used was allylamine; yield: 82%; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C): δ = 4.05 (d, ^3J = 5.5 Hz, 4H; NHCH_2), 4.99 (s, 1H; N=C=CH), 5.17 (m, 2H; CH=CH^1H^2), 5.22 (m, CH=CH$^1H^2$), 5.42 (s, 1H; O=C=CH), 5.84 (ddt, ^3J = 16.9, 10.7, 5.5 Hz, 2H; CH=CH$_2$), 9.25 ppm (brs, 2H; NH); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO, 25°C): δ = 45.25 (s, NHCH$_2$), 82.85 (s, N=C=*C*) 98.09 (s, O=C=*C*), 117.89 (s, CH=*C*H$_2$), 132.60 (s, *C*H=CH$_2$), 156.90 (s, N=C), 172.46 ppm (s, O=C); elemental analysis calcd (%) for C$_{12}$H$_{14}$N$_2$O$_2$·0.5H$_2$O: C 63.42, H 6.65, N 12.33; found: C 63.29, H 6.45, N 12.30; MS (MALDI-TOF$^+$): *m/z*: 219.1 [*M*+1]$^+$.

Ligand 10: A similar procedure was used with the amine 3-amino-1-propanol; yield: 72%; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C): δ = 1.77 (pent, ^3J = 6.4 Hz, 4H; CH_2CH$_2$OH), 3.47 (m, 8H; CH_2OH, CH_2NH), 4.70 (brs, 2H; OH), 4.97 (s, 1H; N=C=CH), 5.52 (s, 1H; O=C=CH), 8.99 ppm (brs, 2H; NH); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO, 25°C): δ = 31.32 (s, *C*H$_2$CH$_2$OH), 40.70 (s, NCH$_2$), 58.85 (s, CH$_2$OH), 81.66 (s, N=C=*C*), 98.02 (s, O=C=*C*), 156.59 (s, N=C), 172.56 ppm (s, O=C); elemental analysis calcd (%) for C$_{12}$H$_{18}$N$_2$O$_4$: C 56.68, H 7.13, N 11.02; found: C 56.35, H 7.23, N 10.79; MS (MALDI-TOF$^-$): *m/z*: 253.1 [*M*−1]$^-$.

Ligand 11: An excess of 3-amino-1,2-propanediol (1.594 g, 17.5 mmol) was added to a suspension of **3**·2HCl (0.533 g, 2.50 mmol) in ethanol (12 mL) and the mixture was then stirred overnight at room temperature. After filtration and washing with cold ethanol, a dark brown powder was obtained. Yield: 89%; ^{1}H NMR (300 MHz, D$_2$O, 25°C): δ = 3.47–3.64 (m, 8H; NHCH_2 and CH_2OH), 3.96 (m, 2H; C*H*OH), 5.26 (s, 1H; N=C=CH), 5.54 ppm (s, 1H; O=C=CH); ^{13}C{^{1}H} NMR (75 MHz, D$_2$O, 25°C): δ = 45.55 (s, NHCH$_2$), 63.13 (s, CH$_2$OH), 69.60 (s, CHOH), 83.00 (s, N=C=*C*), 99.80 (s, O=C=*C*), 156.44 (s, N=C), 175.28 ppm (s, O=C); elemental analysis calcd (%) for C$_{12}$H$_{18}$N$_2$O$_6$: C 50.35, H 6.34, N 9.79; found: C 50.17, H 6.27, N 9.84; MS (MALDI-TOF$^-$): *m/z*: 285.1 [*M*−1]$^-$.

Ligand 12: An excess of serinol (1.594 g, 17.5 mmol) was added to a suspension of **3**·2HCl (0.533 g, 2.50 mmol) in ethanol (12 mL). Then the mixture was refluxed for 6 h. After filtration and washing with cold ethanol, a dark brown powder was obtained. Yield: 85%; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C): δ = 3.61 (t, ^3J = 5.3 Hz, 8H; CH_2OH), 3.85 (pent, ^3J = 5.2 Hz, 2H; NHC*H*), 5.03 (t, ^3J = 5.2 Hz, 5H; N=C=CH and OH), 5.71 (s, 1H; O=C=CH), 8.45 ppm (brs, 2H; NH); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO, 25°C): δ = 57.18 (s, CH$_2$OH), 60.12 (s, CHNH), 82.94 (s, N=C=*C*), 97.54 (s, O=C=*C*), 156.84 (s, N=C), 172.29 ppm (s, O=C); elemental analysis calcd (%) for C$_{12}$H$_{18}$N$_2$O$_6$: C 50.35, H 6.34, N 9.79; found: C 49.71, H 6.34, 10.31; MS (MALDI-TOF$^-$): *m/z*: 285.1 [*M*−1]$^-$.

Ligand 13: An excess of 2-methoxyethylamine (5.258 g, 70 mmol) was added to a solution of **3**·2HCl (2.131 g, 10 mmol) in H$_2$O (20 mL). After 2 h the reaction mixture was extracted by CH$_2$Cl$_2$, the organic layer was collected and dried with MgSO$_4$. After concentration, diethylether was added to the solution and the precipitate was filtered. The purple crystalline solid was obtained after filtration and drying in air. This compound was highly soluble in water and organic solvents and gave purple solutions. Yield: 76%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 3.39 (s, 6H; CH$_3$), 3.53 (t, ^3J = 5.0 Hz, 4H; NHCH$_2$), 3.64 (t, ^3J = 5.0 Hz, 4H; CH$_2$O), 5.23 (s, 1H; N=C=CH), 5.42 (s, 1H; O=C=CH), 8.42 ppm (brs, 2H; NH); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25°C): δ = 43.22 (s, NCH$_2$), 59.14 (s, CH$_3$), 69.37 (s, OCH$_2$), 81.27 (s, N=C=C), 98.77 (s, O=C=C), 157.21 (s, N=C), 172.22 ppm (s, O=C); elemental analysis calcd (%) for C$_{12}$H$_{18}$N$_2$O$_4$: C 56.68, H 7.13, N 11.02; found: C 56.09, H 7.17, N 11.37; MS (MALDI-TOF$^+$): *m/z*: 255.1 [*M*+1]$^+$.

Ligand 14: An excess of ethylenediamine (1.052 g, 17.5 mmol) was added to a suspension of **3**·2HCl (0.533 g, 2.50 mmol) in ethanol (12 mL) and the mixture was stirred for 2 h. After filtration and washing with cold ethanol, a dark brown powder was obtained. This compound was highly soluble in H$_2$O, and resulted in a purple solution. Yield: 86%; ^{1}H NMR (300 MHz, D$_2$O, 25°C): δ = 2.86 (t, ^3J = 6.1 Hz, 4H; CH_2NH$_2$), 3.48 (t, ^3J = 6.1 Hz, 4H; NHCH_2), 5.26 (s, 1H; N=C=CH), 5.48 ppm (s, 1H; O=C=CH); ^{13}C{^{1}H} NMR (75 MHz, D$_2$O, 25°C): δ = 39.08 (s, CH$_2$NH$_2$), 45.23 (s, NHCH$_2$), 82.53 (s, N=C=*C*), 99.89 (s, O=C=*C*), 156.17 (s, N=C), 175.23 ppm (s, O=C); elemental analysis calcd (%) for C$_{10}$H$_{16}$N$_4$O$_2$·1.5H$_2$O: C 47.80, H 7.62, N 22.30; found: C 48.53, H 7.37, N 22.42. Despite several attempts, no better results (C) could be obtained for this compound. MS (MALDI-TOF$^-$): *m/z*: 223.1 [*M*-1]$^-$.

Ligand 16: An excess of *N*-ethylethylenediamine (6.171 g, 70 mmol) was added to a suspension of **3**·2HCl (2.131 g, 10 mmol) in methanol (30 mL). After the reaction mixture was stirred for 2 h, NaOH (2 equiv) were added to the solution, which was then stirred for 0.5 h. After concentration, diethyl ether was added to the solution and the precipitate was filtered. The product was dissolved in dichloromethane, and the solution filtered through Celite. The pale orange brown product was obtained after evaporation of the solvent and precipitation from a mixture of dichloromethane and pentane. This compound was soluble in H$_2$O, alcohol, or CHCl$_3$ and gave purple solutions. Yield: 63%; ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 1.12 (t, ^3J = 7.1 Hz, 6H; CH$_2$CH_3), 2.69 (q, ^3J = 7.1 Hz, 4H; CH_2CH$_3$), 2.97 (t, ^3J = 6.0 Hz, 4H; C=NHCH$_2$CH_2), 3.43 (t, ^3J = 6.0 Hz, 4H; C=NHCH_2), 5.19 (s, 1H; N=C=CH), 5.45 ppm (s, 1H; O=C=CH); ^{13}C NMR (75 MHz, CDCl$_3$, 25°C): δ = 15.32 (s, CH$_3$), 42.98 (s, *C*H$_2$CH$_3$), 43.84 (s, C=NHCH$_2$*C*H$_2$), 47.00 (s, C=NHCH$_2$), 81.19 (s, N=C=*C*), 98.96 (s, O=C=*C*), 156.90 (s, N=C), 172.36 ppm (s, O=C); elemental analysis calcd (%) for C$_{14}$H$_{24}$N$_4$O$_2$·0.5H$_2$O: C 58.11, H 8.71, N19.36; found: C 58.82, H 8.51, N 19.87; MS (MALDI-TOF$^-$): *m/z*: 279.2 [*M*−1]$^-$.

Intermediate D: Although this intermediate was not isolated in the reactions of Scheme 3, it can be obtained by reaction of **6** with LiOH in a THF/H$_2$O mixture, as described for **17** in reference [7]. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 0.96 (t, ^3J = 7.3 Hz, 3H; CH$_3$), 1.42 (m, 2H; CH$_3$CH_2), 1.66 (m, 2H; CH$_3$CH$_2$CH_2), 3.18 (q owing to overlapping dt, ^3J = 6.1 Hz, 2H; NHCH_2), 5.43 (s, 1H; NHC=C*H*), 5.90 (s, 1H; HOC=C*H*), 6.42 (brs, 1H; NH), 8.22 ppm (brs, 1H; OH); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25°C): δ = 13.64 (s, CH$_3$), 20.15 (s, CH$_3$*C*H$_2$), 30.13 (s, CH$_3$CH$_2$*C*H$_2$), 42.58 (s, NHCH$_2$), 92.17 (s, NHC=*C*H), 102.28 (s, HOC=*C*H), 150.01 (s, CNH), 159.37 (s, HOC), 178.13, 182.54 ppm (s, CO); elemental analysis calcd (%) for C$_{10}$H$_{13}$NO$_3$: C 61.53, H 6.71, N 7.18; found: C 61.16, H 6.78, N 7.03; MS (MALDI-TOF$^+$): *m/z*: 196.1 [*M*+1]$^+$.

Ligand 18: Diaminoresorcinol dihydrochloride **3**·2HCl (0.500 g, 2.35 mmol) was dissolved in water and excess of *n*-butylamine was added to the solution. The reaction mixture was allowed to stand for 3 days to afford a red crystalline solid. Yield: 71%; ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 0.95 (t, ^3J = 7.4 Hz, 6H; CH$_3$), 1.40 (sext, ^3J = 7.4 Hz, 4H; CH$_3$CH_2), 1.64 (pent, ^3J = 7.4 Hz, 4H; CH$_3$CH$_2$CH_2), 3.15 (q owing to overlapping dt, ^3J = 6.6 Hz, 4H; NHCH_2), 5.30 (s, 2H; CH), 6.60 ppm (brs, 2H; NH); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25°C): δ = 13.66 (s, CH$_3$), 20.17 (s, CH$_3$CH$_2$), 30.25 (s, CH$_3$CH$_2$*C*H$_2$), 42.30 (s, NHCH$_2$), 92.64 (s, CH), 151.36 (s, *C*NH), 178.13 ppm (s, CO); elemental analysis calcd (%) for C$_{14}$H$_{22}$N$_2$O$_2$·0.25H$_2$O: C 65.98, H 8.90, N 10.99; found: C 66.08, H 8.78, N 10.96; MS (MALDI-TOF$^+$): *m/z*: 251.2 [*M*+1]$^+$.

Complex 19: Ligand **13** (0.20 g, 0.787 mmol) was dissolved in anhydrous dichloromethane (50 mL) and Zn(acac)$_2$ (0.5 equiv) was added to the solution. After the solution was stirred at room temperature for 3 h, the solvent was evaporated and the red, crystalline complex **19** was obtained by precipitation from a mixture of dichloromethane and pentane. Yield: 87%; ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 3.16 (s, 6H; uncoordinated OCH$_3$), 3.35 (q, ^3J = 5.5 Hz, 4H; NHCH_2), 3.38 (s, coordinated OCH$_3$), 3.61 (m, 12H; NCH$_2$ and OCH$_2$), 5.13 (s, 2H; N=CCH), 5.58 (s, 2H; O=CCH), 6.93 ppm (t, ^3J = 5.5 Hz, 2H; NH); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25°C): δ = 42.43 (s, uncoordinated OCH$_3$), 47.12 (s, coordinated OCH$_3$), 58.57 (s, CH$_2$), 59.05 (s, CH$_2$), 69.69 (s, CH$_2$), 70.09 (s, CH$_2$), 82.87 (s, NHC=*C*H), 101.22 (s, O=C*C*H), 149.67 (s, NHC), 161.78 (s, COZn), 173.43 (s, C=NZn), 179.20 ppm (s, C=O); elemental analysis calcd (%) for C$_{24}$H$_{34}$N$_4$O$_8$Zn: C 50.40, H 5.99, N 9.80; found: C 49.76, H 6.01, N 9.49; MS (MALDI-TOF$^+$): *m/z*: 570.2 [*M*]$^+$.

Complex 21: The procedure used was similar to that described for **19**, but using ligand **16** instead of **13**. Yield: 71%; ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 1.02 (t, ^3J = 7.1 Hz, 6H; uncoordinated NHCH$_2$CH_3), 1.11 (t, ^3J = 7.1 Hz, 6H; coordinated NHCH$_2$CH_3), 2.64 (m, 8H; CH$_2$), 2.90 (brt, 8H; CH$_2$), 3.29 (q, ^3J = 5.9 Hz, 4H; CH$_2$), 3.46 (brt, 4H; CH$_2$), 5.11 (s,

2H; NHC=C*H*), 5.48 (s, 2H; O=CC*H*), 6.87 ppm (t, ^3J=5.5 Hz, 2H; N*H*C=CH); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ=14.55 (s, uncoordinated $NHCH_2CH_3$), 15.33 (s, coordinated $NHCH_2CH_3$), 42.42 (s, uncoordinated $NHCH_2CH_3$), 43.99 (s, coordinated $NHCH_2CH_3$), 44.08 (s, uncoordinated $CH_2NHCH_2CH_3$), 45.63 (s, coordinated $CH_2NHCH_2CH_3$), 47.62 (s, uncoordinated $CH_2NHCH_2CH_2$), 48.10 (s, coordinated C=NCH_2), 83.17 (s, NHC=*C*H), 100.47 (s, O=C*C*H), 149.87 (s, NHC), 159.80 (s, COZn), 173.93 (s, C=NZn), 178.76 ppm (s, C=O); elemental analysis calcd (%) for $C_{28}H_{46}N_8O_4Zn$: C 53.98, H 7.43, N 17.95; found: C 53.60, H 7.50, N 17.96; MS (MALDI-TOF$^+$): *m/z*: 623.3 $[M+1]^+$.

Complex 22: A solution of **15** (100 mg) in methanol (10 mL) was slowly added to $ZnCl_2$ (1 equiv) in methanol (5 mL). After stirring for 1 h, filtration, washing with methanol and drying in air, a red powder was obtained. Single crystals suitable for X-ray analysis were obtained from a slow reaction between $ZnCl_2$ and the ligand in methanol (i.e. a solution of ligand was slowly added to the solution of $ZnCl_2$). Yield: 76%; ^{1}H NMR (300 MHz, D_2O, 25 °C): δ=2.40 (br, 6H; Me_2NZr), 2.78 (br, 2H; CH_2), 2.86 (br, 6H; Me_2NH), 3.36 (br, 2H; CH_2), 3.60 (br with sh, 4H; $2CH_2$), 5.34 ppm (br, 2H; CH); the signal for the CH protons splits at 65 °C into two singlets at δ=5.82 and 5.83 ppm; elemental analysis calcd (%) for $C_{14}H_{24}Cl_2N_4O_2Zn$: C 40.36, H 5.81, N 13.45; found: C 40.19, H 6.00, N 13.28; MS (MALDI-TOF$^-$): *m/z*: 415.0 $[M-1]^-$.

Complex 23: The procedure used for the preparation and crystallization was similar to that described for **22**, but with ligand **16** instead of **15**. Yield: 77%; ^{1}H NMR (300 MHz, D_2O, 25 °C): δ=0.90 (br, 3H; CH_3CH_2NZn), 1.22 (t, ^3J=7.2 Hz, CH_3CH_2NH), 2.53 (br, 2H; CH_2), 2.94 (br, 2H; CH_2), 3.06 (q, ^3J=7.2 Hz, CH_3CH_2NH), 3.26 (br, 2H; CH_2), 3.59 (br with sh, 4H; $2CH_2$), 5.34 (s, 1H; N=C=CH), 5.44 ppm (s, 1H; O=C=CH); elemental analysis calcd (%) for $C_{14}H_{24}Cl_2N_4O_2Zn$: C 40.36, H 5.81, N 13.45; found: C 39.74, H 5.89, N 13.04; MS (MALDI-TOF$^-$): *m/z*: 415.0 $[M-1]^-$.

X-ray data: The selected single crystals were mounted on a Nonius Kappa-CCD area-detector diffractometer. The complete conditions of data collection (Denzo software) and structure refinements are given in Table 5. The structures were solved by using direct methods (SIR97) and refined against F^2 by using the SHELXL97 software. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.[22] CCDC 273367–273370 (**4**·H_2O, **5**·H_2O, **13**, and **15**, respectively) and CCDC 267838 and 267839 (**22** and **23**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The supporting information for this article contains a description of the molecular packing in **4**·H_2O and **5**·H_2O and the cif file for the crystal structure of **5**, which could not be fully refined and was therefore not deposited with CCDC.

Acknowledgements

This work was supported by the Centre National de la Recherche Scientifique and we are grateful to the Ministère de la Recherche et des Nouvelles Technologies and Clariant for a postdoctoral grant to Q.-Z.Y. We are grateful to Prof. R. Welter and Dr. A. DeCian for the determination of the crystal structures and wish to thank a referee for the details of references [20] and [21].

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Table 5. Crystal data and details of the structure determination for compounds **4**·H_2O, **5**·H_2O, **13**, **15**, **22**, and **23**.

	4·H_2O	**5**·H_2O	**13**	**15**	**22**	**23**
formula	$C_6H_8N_2O_3$	$C_8H_{12}N_2O_3$	$C_{12}H_{18}N_2O_4$	$C_{14}H_{24}N_4O_2$	$C_{14}H_{24}N_4O_2Zn_2Cl_2$	$C_{14}H_{24}N_4O_2Zn_2Cl_2$
M_r	156.14	184.20	254.28	280.37	416.64	416.64
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	*Pnma*	*C*2/*c*	$P2_1/n$	$P2_1/c$
a [Å]	3.6540(3)	7.3470(10)	8.5800(3)	29.9490(9)	7.683(5)	10.2640(4)
b [Å]	14.4280(12)	8.8780(10)	14.7120(4)	7.3910(3)	9.938(5)	13.2900(5)
c [Å]	12.6590(9)	13.967(2)	10.6120(8)	6.9050(2)	22.846(5)	13.4400(6)
β [°]	95.270(5)	96.27(5)	90	98.430(2)	92.91(5)	94.2350(14)
V [Å^3]	664.56(9)	905.6(2)	1339.54(12)	1511.93(9)	1742.1(15)	1828.33(13)
Z	4	4	4	4	4	4
ρ [g cm^{-3}]	1.561	1.351	1.261	1.232	1.589	1.514
T [K]	173(2)	293(2)	173(2)	173(2)	173(2)	173(2)
λ [Å]	0.71070	0.71070	0.71073	0.71070	0.71069	0.71073
reflns collected	1915	2643	2212	2196	5089	5243
independent reflns	1296	1697	1491	1456	3302	3638
*R*1/*wR*2 [$I>2\sigma(I)$]	0.0933/0.1303	0.0598/0.1406	0.0453/0.1119	0.0495/0.1392	0.0372/0.0905	0.1418/0.2006
*R*1, *wR*2 (all data)	0.1584/0.1472	0.1017/0.1605	0.0768/0.1257	0.0830/0.1613	0.0691/0.1008	0.1985/0.2191

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Received: June 20, 2005
Published online: September 30, 2005

