Mononuclear zinc(II) complexes of *o*-amino phenolate ligands. X-Ray structure of the zwitterionic [ZnCl$_2$L] compound with 2,6-bis(dimethylaminomethyl)-4-*tert*-butylphenol

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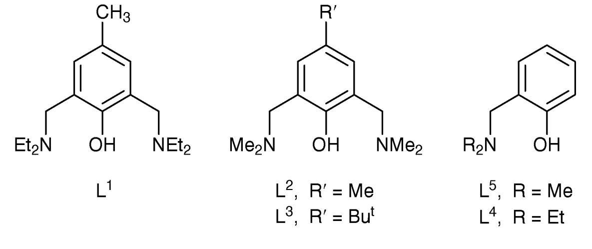
Reaction of 2,6-bis(dialkylaminomethyl)-4-alkylphenols (L) with ZnCl$_2$ in ethanol leads to zwitterionic Zn(II) complexes [ZnCl$_2$L]. An X-ray diffraction study on the compound with L = 2,6-bis(dimethylaminomethyl)-4-*tert*-butylphenol reveals the presence of a mononuclear zincate complex, in which the distorted tetrahedral coordination of the metal consists of two chlorine atoms and the ligand L acting as a bidentate chelating agent *via* the deprotonated phenol oxygen and one amino group. Migration of the phenolic hydrogen to the uncoordinated amino group in the other *ortho* substituent generates an ammonium group whose positive charge balances the negative charge of the zincate centre. This ammonium group forms an intramolecular N—H···O hydrogen bond with the coordinated phenoxide oxygen. Complex stability is enhanced by the reduction of electron density accompanying the formation of the phenoxide 'bridge' between the Zn atom and the ammonium proton. ^{1}H and ^{13}C NMR spectroscopies indicate that ligand dissociation does not occur and the complexes retain their solid-state structure in solution.

Zinc(II) is known to coordinate to a variety of ligands, forming tetra-, penta- and hexacoordinate mononuclear complexes whose applications in materials sciences[1] and as models for enzyme substrates[2] are well-documented. In contrast, the reactions with alkoxides and phenoxides have been found to lead mainly to dinuclear complexes or higher oligomers, the monomeric species remaining very uncommon.[3–7] This is a behaviour generally observed for alkoxide and phenoxide compounds with M^{2+} ions, in which oxide bridging favors the delocalisation of electron density over two or more metal centres. In agreement with this generalisation, dimeric molecules are found to be produced when ZnR$_2$ is reacted with L^5 (Scheme 1).[8] On the other hand, ZnCl$_2$ reacts with L^4 in the presence of a base (NEt$_3$) to give the monomeric zincate complex (HNEt$_3$)[ZnCl$_2$L^4] as an ion pair soluble in many organic solvents.[9] Ion pairing, which takes place *via* strong hydrogen bonding between the zinc-coordinated phenolate oxygen and the triethylammonium ion, competes with the oligomerisation processes and stabilises the monomeric species. Since it is well-known that monomeric Zn^{II} complexes are stabilised by chelation with tri- and tetradentate ligands,[10,11] it could be reasonably assumed that phenoxide ligands containing one or two potentially coordinating amine substituents in *ortho* positions would act similarly.



Scheme 1

We wish to report our results on the reaction of ZnCl$_2$ with the potentially tridentate macrocyclic ligands L^1, L^2 and L^3 derived from L^4- and L^5-type molecules by adding a dialkylaminomethyl substituent at the other *ortho* position (Scheme 1). The presence of a second —CH$_2$NR$_2$ substituent increases the steric effect around the Zn centre, but its Lewis basicity could be used to form an extra intramolecular bond with a metal ion or other Lewis acid without losing the original coordination pattern around Zn. Thus, the major questions raised by the present systems were the role the extra amino-substituted side-chain would play and what the nuclearity of the resulting Zn^{II} complexes would be.

Experimental

2,6-Bis(diethylaminomethyl)-4-methylphenol (L^1), 2,6-bis(dimethylaminomethyl)-4-methylphenol (L^2) and 2,6-bis(dimethyl aminomethyl)-4-*tert*-butylphenol (L^3) were synthesised by the standard literature method.[12] Commercial ZnCl$_2$ (Aldrich) was dried by heating at 80 °C in vacuum for 1 h. Freshly distilled ethanol was used for all syntheses.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in CDCl$_3$ solutions at room temperature with a Bruker AMX-R-400 spectrometer. Residual solvent signals (^{1}H 7.27, ^{13}C 77.23 ppm) were used as internal standards and the chemical shifts (δ) are reported with respect to Me$_4$Si. Mass spectra were

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Table 1 ^1H and $^{13}C\{^1H\}$ NMR data for complexes **1**, **2** and **3** (RT, $CDCl_3$)

Complex		δ^a
1	^1H	1.08 (t, 6H, CH_3, $^3J_{HH_a} = {}^3J_{HH_{a'}} = 7.1$ Hz); 1.36 (t, 6H, CH_3, $^3J_{HH} = 7.3$ Hz); 2.16 (s, 3H, CH_3); 2.55 (dq, 2H, H_a, $^2J_{HH} = 14.6$; $^3J_{HH} = 7.0$ Hz)[b]; 3.08 (m, 6H, H_b, $H_{a'}$, $H_{b'}$)[b]; 3.70 (s, 2H, CH_2); 4.08 (d, 2H, CH_2, $J_{HH} = 3$ Hz); 6.76 (d, 1H, $^4J_{HH} = 1.8$ Hz); 6.82 (d, 1H, $^4J_{HH} = 1.9$ Hz); 10.85 (br s, 1H)
	^{13}C	8.2 (CH_3, C_{11}); 9.1 (CH_3, C_{13}); 20.4 (CH_3, C_9); 44.9 (CH_2, C_{10}); 46.7 (CH_2, C_{12}); 56.6 (CH_2, C_7); 57.0 (CH_2, C_8); 117.1, 122.5 (C, C_2,C_6) 124.4 (C, C_4); 130.3, 133.2 (CH, C_3, C_5); 161.5 (CO, C_1)
2	^1H	2.16 (s, 3H, CH_3); 2.43 (s, 6H, CH_3); 2.82 (s, 6H, CH_3); 3.60 (s, 2H, CH_2); 4.08 (s, 2H, CH_2); 6.79 (s, 1H); 6.82 (s,1H); 10.5 (vbr s, 1H, NH)
	^{13}C	20.2 (CH_3, C_9); 43.3 (CH_3, C_{11}); 47.4 (CH_3, C_{13}); 62.7 (CH_2, C_7); 63.2 (CH_2, C_8); 118.1, 123.5, (C, C_2, C_6); 127.7 (C, C_4); 130.1, 133.9 (CH, C_3, C_5); 161.5 (CO, C_1)
3	^1H	1.18 (s, 9H, CH_3); 2.39 (s, 6H, CH_3);2.82 (s, 6H, CH_3); 3.60 (s, 2H, CH_2); 4.14 (s, 2H, CH_2); 6.97 (br s, 2H, CH); 10.3 (vbr s, 1H, NH)
	^{13}C	36.1 (CH_3, C'_9); 33.7 (C, C_9); 43.1 (CH_3, C_{11}); 47.3 (CH_3, C_{13}); 62.7 (CH_2, C_7); 63.6 (CH_2, C_8); 117.0, 122.6 (C, C_2, C_6); 127.1, 129.2 (CH, C_3, C_5); 138.3 (C, C_4); 161.0 (CO, C_1)

[a] Abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, dq = doublet of quadruplets, m = multiplet, br = broad, vbr = very broad.
[b] The non-equivalent protons in the ethyl CH_2 group are represented by H_a and $H_{a'}$ (arm A) and H_b and $H_{b'}$ (arm B).

recorded using the DCI-NH_3 and FAB^+ techniques on a NERMAG *R* 1010 spectrometer. Microanalyses were carried out at the Service Central de Microanalyses du CNRS, Lyon, and the Service de Microanalyses du LCC, Toulouse.

Syntheses

Dichloro[2-(diethylaminomethyl)-6-(diethylammoniummethyl)-4-methylphenolato]zincate (1). An ethanol solution (20 mL) containing 0.59 g (4.3 mmol) of anhydrous $ZnCl_2$ was added dropwise to the ligand L^1 (1.9 g, 4.3 mmol) dissolved in ethanol (20 mL). A white solid began to precipitate after 10 min and stirring was continued for 30 min. The solid was filtered off and recrystallised from hot ethanol to give tiny crystals of the product in nearly quantitative yield. Anal: calcd % (found) for $C_{17}H_{30}Cl_2N_2OZn$: C, 49.23 (48.80); H, 7.29 (7.37); N, 6.75 (6.67). Mass spectrum (*m*/*z*), DCI-NH_3: 415 $[M + H]^+$, 377 $[M + H - HCl]^+$, 279 $[L^1 + H]^+$. ^1H and ^{13}C NMR (see Table 1).

Dichloro[2-(dimethylaminomethyl)-6-(dimethylammoniummethyl)-4-methylphenolato]zincate (2). In a similar manner, anhydrous $ZnCl_2$ (0.94 g, 6.9 mmol) and L^2 (1.5 g, 6.9 mmol) in ethanol gave complex **2** as a white crystalline solid in nearly quantitative yield. Anal: calcd % (found) for $C_{13}H_{22}Cl_2N_2OZn \cdot 0.5C_2H_5OH$: C, 44.06 (44.30); H, 6.60 (5.58); N, 7.34 (7.34). Mass spectrum (*m*/*z*), FAB^+: 358 $[M]^+$. ^1H and ^{13}C NMR (see Table 1).

Dichloro[2-(dimethylaminomethyl)-6-(dimethylammoniummethyl)-4-*tert*-butylphenolato]zincate (3). By the above procedure, L^3 (1.02 g, 3.8 mmol) and anhydrous $ZnCl_2$ (0.53 g, 3.8 mmol) gave an essentially quantitative yield of **3**. Crystals suitable for X-ray diffraction work precipitated overnight from the saturated solution left at 0 °C. Anal: calcd % (found) for $C_{16}H_{28}Cl_2N_2OZn$: C, 47.95 (47.65); H, 7.04 (7.16); N, 6.99 (6.87). Mass spectrum (*m*/*z*), FAB^+: 400 $[M]^+$. ^1H and ^{13}C NMR (see Table 1).

X-Ray diffraction study on compound 3

The X-ray work was carried out at low temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatised MoKα radiation. The reduced cell deduced from 25 reflections observed on a rotation photograph corresponded to a primitive monoclinic lattice. At a later stage, the $2/m$ Laue symmetry was checked from the full data set and the space group $P2_1/c$ was identified unambiguously from the systematic absences. The crystallographic data are summarised in Table 2.

The intensities were measured by the $\omega/2\theta$ scan technique, with a scan range $\Delta\omega$ of $(1.00 + 0.35 \tan\theta)°$ and a constant scan rate of 16.5° min^{-1}. The orientation was checked every 400 measurements, whereas the intensity was monitored every hour with three standard reflections. Intensity fluctuations remained within ±2.6%. A total of 5838 *hkl* and $\bar{h}kl$ reflections were collected. Equivalent reflections were averaged and the corrections for the Lorentz and polarization effects were applied. The data were not corrected for absorption, considering the very small absorption coefficient ($\mu = 1.50$ mm^{-1}) and crystal size. The final data set consisted of 5585 independent reflections, of which 3775 with $I > 2\sigma(I)$ were retained for the structure determination.

The structure was solved by direct methods using SHELXS-86[13] and ΔF syntheses. Least-squares refinement was done on F^2 with SHELXL-96.[14] All non-hydrogen atoms were refined anisotropically. Hydrogens were initially introduced at idealised positions and refined isotropically in the last cycles. Convergence was reached for an *R* value of 0.0322. The final ΔF map showed a general background within ± 0.15 e $Å^{-3}$ and a few residuals of $\pm\lvert 0.30\text{–}0.55 \rvert$ e $Å^{-3}$ near the Zn and Cl atoms.

CCDC reference number 440/047.

Table 2 Crystallographic data for compound **3**

Formula	$C_{16}H_{28}Cl_2N_2OZn$
Formula weight	400.68
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.505(2)
b/Å	10.852(2)
c/Å	15.663(2)
β/°	100.35(2)
U/Å^3	1923.7(5)
Z	4
D_{calc}/g cm^{-3}	1.383
Radiation type	MoKα
λ/Å	0.71073
μ/mm^{-1}	1.59
Temperature/K	173(2)
No. measured reflections	5838
No. independent reflections	5585
No. reflections with $I > 2\sigma(I)$	3775
$2\theta_{max}$/°	60.0
R_1[a]	0.0322
wR_2[a]	0.0836

[a] $R_1 = \Sigma(\lVert F_o\rvert - \lvert F_c\rVert)\Sigma\lvert F_o\rvert$, $wR_2 = \{\Sigma[w(\lvert F_o\rvert - \lvert F_c\rvert)^2]/\Sigma[w\lvert F_o\rvert^2]\}^{1/2}$

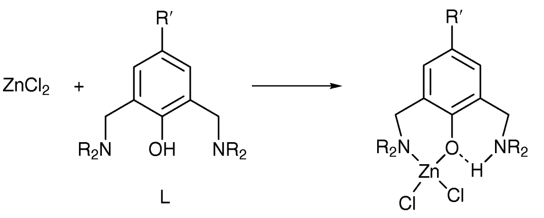
Results

Complexes **1**, **2** and **3** were obtained by mixing equimolar amounts of $ZnCl_2$ and the appropriate ligand in ethanol (Scheme 2). They are air-stable, colourless crystalline powders, soluble in most organic solvents. Elemental analyses and mass spectra are in agreement with the formula $ZnCl_2L$.

X-Ray diffraction study

These complexes were identified as mononuclear zwitterionic species by performing a crystal structure determination on single crystals of compound **3**. An ORTEP drawing including the atomic numbering scheme is given in Fig. 1. Bond lengths and angles are listed in Table 3.

The zinc atom is in a distorted tetrahedral coordination environment, bonded to two chlorine atoms and to the L^3 ligand, thus forming a chelate ring *via* the deprotonated phenolato oxygen and the nitrogen atom of one of the $-CH_2N(CH_3)_2$ arms. The phenol proton has been shifted to the nitrogen atom in the other arm, thereby generating a positively charged ammonium group that balances the negative charge of the Zn coordination sphere. This cationic group forms an intramolecular hydrogen bond with the coordinated phenolate oxygen. The hydrogen bond is fairly strong, with the N(8)—O(1) distance [2.730(2) Å] lying on the low side of the range (2.57–3.22 Å) considered by Stout and Jensen for this type of hydrogen bond,[15] although the deviation from linearity is relatively large [N(8)—H—O(1) = 137(2)°]. A related situation has been met with the $(HNEt_3)[ZnCl_2L^4]$ complex, in which the phenolate ligand L^4 possesses a single $-CH_2N(C_2H_5)_2$ arm.[9] In the latter case, a similar negatively charged $[ZnCl_2(O{\cap}N)]^-$ coordination is achieved around the metal and ion pairing with $(HNEt_3)^+$ takes place *via* hydrogen bonding with the coordinated phenolate oxygen. In the present compound, the $(ZnCl_2(O{\cap}N)]^-$ and the ammonium units belong to the same molecule and hydrogen bonding takes place internally.



L = L^1 = 2,6-bis(diethylaminomethyl)-4-methylphenol **(1)**
L = L^2 = 2,6-bis(dimethylaminomethyl)-4-methylphenol **(2)**
L = L^3 = 2,6-bis(dimethylaminomethyl)-4-*tert*-butylphenol **(3)**

Scheme 2

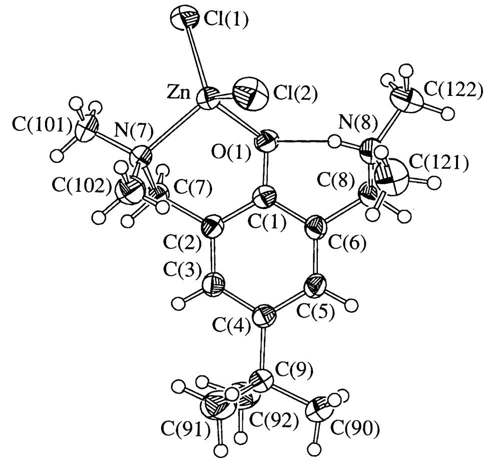


Fig. 1 ORTEP drawing of the $[ZnCl_2L^3]$ molecule (**3**). Ellipsoids are drawn at the 50% probability level. Hydrogens are shown as small spheres of arbitrary size. The thin line corresponds to the N—H···O hydrogen bond

The bonds around the metal are typical of single Zn—Cl, Zn—O and Zn—N bonds in a tetrahedral environment and are very close to those found in $(HNEt_3)[ZnCl_2L^4]$.[9] The O—Zn—N angle [98.96(6)°], which is largely controlled by

Table 3 Interatomic distances (Å) and bond angles (deg)

Zn—O(1)	1.9436(13)	Zn—N(7)	2.091(2)
Zn—Cl(1)	2.2212(6)	Zn—Cl(2)	2.2430(7)
O(1)—C(1)	1.331(2)	N(7)—C(7)	1.497(2)
N(7)—C(101)	1.475(2)	N(7)—C(102)	1.468(3)
N(8)—C(8)	1.514(3)	N(8)—C(121)	1.471(3)
N(8)—C(122)	1.486(3)	C(1)—C(6)	1.400(2)
C(1)—C(2)	1.409(2)	C(2)—C(3)	1.388(3)
C(2)—C(7)	1.499(2)	C(3)—C(4)	1.396(2)
C(4)—C(5)	1.393(2)	C(4)—C(9)	1.533(3)
C(5)—C(6)	1.390(3)	C(6)—C(8)	1.502(3)
C(9)—C(90)	1.525(3)	C(9)—C(91)	1.520(3)
C(9)—C(92)	1.535(4)		
O(1)—Zn—N(7)	98.96(6)	O(1)—Zn—Cl(1)	112.58(4)
N(7)—Zn—Cl(1)	110.87(4)	O(1)—Zn—Cl(2)	100.84(4)
N(7)—Zn—Cl(2)	112.08(5)	Cl(1)—Zn—Cl(2)	119.23(3)
C(1)—O(1)—Zn	117.78(10)	C(7)—N(7)—C(101)	108.1(2)
C(7)—N(7)—C(102)	110.5(2)	C(101)—N(7)—C(102)	108.8(2)
C(102)—N(7)—Zn	113.52(14)	C(101)—N(7)—Zn	110.89(12)
C(7)—N(7)—Zn	104.91(11)	C(121)—N(8)—C(122)	111.8(2)
C(8)—N(8)—C(121)	111.3(2)	C(8)—N(8)—C(122)	112.0(2)
O(1)—C(1)—C(6)	119.5(2)	O(1)—C(1)—C(2)	122.2(2)
C(6)—C(1)—C(2)	118.3(2)	C(3)—C(2)—C(1)	119.2(2)
C(3)—C(2)—C(7)	121.0(2)	C(1)—C(2)—C(7)	119.7(2)
C(2)—C(3)—C(4)	123.2(2)	C(5)—C(4)—C(3)	116.6(2)
C(5)—C(4)—C(9)	123.8(2)	C(3)—C(4)—C(9)	119.6(2)
C(6)—C(5)—C(4)	121.7(2)	C(5)—C(6)—C(1)	120.9(2)
C(5)—C(6)—C(8)	122.5(2)	C(1)—C(6)—C(8)	116.6(2)
N(7)—C(7)—C(2)	114.00(14)	C(90)—C(9)—C(91)	108.9(2)
C(4)—C(9)—C(91)	110.0(2)	C(4)—C(9)—C(90)	112.5(2)
C(91)—C(9)—C(92)	108.7(3)	C(90)—C(9)—C(92)	107.6(2)
C(4)—C(9)—C(92)	109.0(2)	C(6)—C(8)—N(8)	110.2(2)

the bite of the ligand, agrees with the one found in the above complex. Other relatively large deviations from tetrahedral geometry are found (Table 3), namely for the Cl—Zn—Cl angle [119.23(3)°], which is balanced by the small O(1)—Zn—Cl(2) angle of 100.84(4)°. The remaining angles show differences $\leqslant 2.2°$ between the two structures. Differences are to be expected since the formation of the *intramolecular* N—H···O interaction likely introduces constraints that disappear when the hydrogen-bonded units are not covalently linked in the same molecule.

The torsion angles collected in Table 4 show that the six-membered chelate ring adopts an approximate boat conformation. In an idealised boat conformer, the sequence of torsion angles would be 60°/0°/−60°/60°/0°/−60°. The values in Table 4 (42°/3°/−64°/61°/−18°/−30°) correspond to a rather large distortion, which is not surprising however, considering the disparity in bond lengths around the ring and the presence of both sp^2 (aromatic ring) and sp^3 (side-arm) hybridised atoms.

Two geometrical features of the ligand deserve comments. Van Koten and coworkers have pointed out that non-deprotonated phenol groups coordinated to Na^+ show C—O distances (1.372 Å) appreciably greater than coordinated phenolate groups (1.301 Å).[20b] The C—O distance of 1.331(2) Å in **3** is about halfway between these two values, probably because the ionic character of the Zn—O bond is between these two extremes. On the other hand, the mean of the C—N—C angles in the uncoordinated $-CH_2NEt_2$ group (111.7°) is appreciably greater than that in the coordinated one (109.1°). The latter value is consistent with the results of a survey of 23 crystal structures of compounds with phenol ligands containing one or two *ortho* $-CH_2NMe_2$ substituents.[16] Uncoordinated and metal-coordinated groups were considered separately, but the same average value of 108.9° was obtained for both samples. On the other hand, in recent crystallographic results on $ReOClL^4(PPh_3)_2$[17] and CuL^1_2Cl,[16] in which uncoordinated $-CH_2NR_2$ groups can be unambiguously shown to be protonated, the mean C—N—C angles are 112.4° and 112.6°, respectively. Therefore, protonation tends to increase the mean C—N—C angle by $\approx 3°$, and from the value of 111.7° observed for the present Zn compound, the uncoordinated side-arm can be safely regarded as protonated.

The remaining distances and angles in the ligand are normal. The aromatic ring is planar within 0.006 Å, but the substituents show relatively large, although not unreasonable, deviations from this plane: C(7), 0.054(3); C(8), 0.069(3); C(9), 0.054(3) Å.

Spectroscopic studies

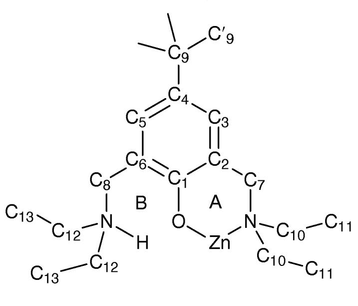
Chemical analysis and mass spectrometry are consistent with L^1, L^2 and L^3 forming the same type of complexes. The DCI-NH_3 mass spectrum of **1** exhibits major peaks at *m*/*z* values of 415 and 377, corresponding to the $[M + H]^+$ and $[M + H - HCl]^+$ fragments, respectively. The FAB^+ spectra for **2** and **3** show the molecular fragments $[M]^+$ at 358 and 400, respectively.

^1H and $^{13}C\{^1H\}$ NMR spectroscopies in $CDCl_3$ at room temperature provide evidence that the solid-state structure of **3** is retained in solution, **1** and **2** adopt similar structures, and the complexes are stable toward ligand dissociation. The data are collected in Table 1 and the numbering scheme is given in Scheme 3.

The $N-H^+$ signal appears clearly at 10.8 ppm on the ^1H NMR spectrum of **1**, while broader singlets appear at 10.5 ppm for **2** and 10.3 ppm for **3**, in the region expected for an ammonium hydrogen involved in hydrogen bonding.

Complexes **2** and **3**, in which the ligand substituents are $-CH_2N(CH_3)_2$, give very similar ^1H NMR spectra. The singlets at 6.79 and 6.82 ppm for **2**, which become a broad signal at 6.97 ppm for **3**, are safely assigned to the two aromatic protons, whereas the singlets at 2.16 ppm in **2** and 1.18 ppm in **3** originate from the 4-methyl and 4-*tert*-butyl groups, respectively. The inequivalence of the two $-CH_2N(CH_3)_2$ arms is obvious in the two spectra. The broad singlets at ≈ 2.43 and 2.82 ppm in **2** and at 2.39 and 2.82 ppm in **3** are assigned to the methyl groups in arms A and B, respectively, while the CH_2 groups appear at 3.60 (A) and ≈ 4.08 ppm (B) in **2** and at 3.60 (A) and 4.14 ppm (B) in **3**. In the solid, the $Zn-O-C_1-C_2-C_7-N$ and $H-O-C_1-C_6-C_8-N$ rings are puckered, and there are inequivalences between the two CH_3 groups and between the two CH_2 protons. Since a single resonance is observed for each of these groups, exchange between the two equivalent mirror-related conformations is fast on the NMR timescale.

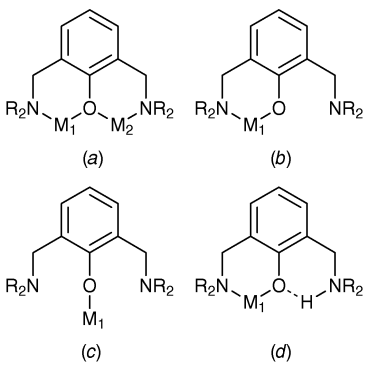
Complex **1**, where the ligand L^1 contains N-bonded ethyl substituents, gives a more complex spectrum. Nevertheless, all signals could be assigned on the basis of decoupling experiments and comparisons with results on $(HNEt_3)[ZnCl_2L^4]$.[9] Again, the rings are non-rigid on the NMR timescale, producing averaged signals for the two ethyl groups and for the two protons in the α-CH_2 groups next to the phenyl ring. However, the two CH_2 protons in the ethyl group are inequivalent. The doublet of quartets at 2.55 ppm is assigned to one of these protons (H_a) in arm A, which is thus coupled with the adjacent methyl protons and with the geminal proton $H_{a'}$. Irradiation of H_a changes the high-field methyl triplet at 1.08 ppm into a doublet, thereby identifying this signal as that of the adjacent methyl group. The complicated signal at 3.08 ppm, which integrates for six protons, was also modified by irradiation, showing a contribution from the $H_{a'}$ protons to this region. Complexation to zinc resulted in a substantial upfield shift for H_a, likely related to its being located close to the electronegative Cl atom. The signal at 3.08 ppm is broad, ill-resolved and difficult to analyse, but it definitely includes, besides $H_{a'}$, the two inequivalent methylene protons H_b and $H_{b'}$ of the ethyl groups in arm B. The resonance of the α-methylene protons (on C_7 and C_8) occurs as a singlet at 3.70



Scheme 3

Table 4 Selected torsion angles (°)

Zn—O(1)—C(1)—C(2)	42.1(2)	C(2)—C(7)—N(7)—Zn	60.9(2)
O(1)—C(1)—C(2)—C(7)	2.7(3)	C(7)—N(7)—Zn—O(1)	−18.2(1)
C(1)—C(2)—C(7)—N(7)	−64.4(2)	N(7)—Zn—O(1)—C(1)	−30.2(1)
HN(8)—O(1)—C(1)—C(6)	−45(2)	C(6)—C(8)—N(8)—HN(8)	−35(2)
O(1)—C(1)—C(6)—C(8)	10.5(3)	C(8)—N(8)—HN(8)—O(1)	−25(2)
C(1)—C(6)—C(8)—N(8)	49.6(2)	N(8)—HN(8)—O(1)—C(1)	76(3)



Scheme 4

ppm in arm A, but a doublet is observed at 4.08 ppm for arm B, as a result of coupling with the ammonium hydrogen. Such couplings are sometimes observed when the N—H protons are involved in strong hydrogen bonding[18] as is apparently the case here. The absence of such couplings for **2** and **3**, together with the much broader low-field N—H signal, suggests that exchange is faster when the amine is methyl-substituted. It is noteworthy that in the three complexes, the protons in the Zn-bonded arm are less downfield shifted than those in the ammonium part, in agreement with the acidity of H^+ being greater than that of Zn^{2+}.[19]

The $^{13}C\{^1H\}$ NMR signals observed for the three complexes are listed in Table 1. All carbon atoms give distinct signals, thereby confirming the monomeric structures in solution. The number and position of the signals are similar for the different complexes and consistent with the ^1H NMR data. As noticed for the protons, and for the same reasons, larger downfield shifts are observed for the carbon atoms located near to the ammonium group than for those bonded to zinc.

Discussion

Reacting $ZnCl_2$ with 2-(dialkylaminomethyl)phenol (L^4) and 2,6-bis(dialkylaminomethyl)phenols (L^1–L^3) gives mononuclear zinc complexes containing anionic zincate centres. The negative charge is balanced by an ammonium cation resulting either from intermolecular migration of the acidic phenol hydrogen to NEt_3 added as a base in the reaction with L^4 or from an intramolecular hydrogen shift to the second amino group with L^1, L^2 and L^3. The description of these compounds as zwitterionic species (acidic proton on N) rather than aminophenol complexes (proton on O) is strongly supported by the X-ray data on **3** and the ^1H NMR results for **1**.

Inspection of the structural results on the complexes with ligands L^2 and L^4 reveals large deviations from the tetrahedral geometry. This is a good illustration of the ability of zinc to distort its filled d shell to accommodate the particular requirements of the ligand in terms of size, electrostatic forces and covalent bonding.

Scheme 4 describes the different coordination modes found in the literature for metal-bonded 2,6-bis(dialkylaminomethyl) phenols. Examples of patterns *a*, *b* and *c* have already been reported.[20] The zwitterionic and ion-pair compounds discussed here are examples of a novel bridging mode *d*, with the phenolate group bridging not two metal atoms as usually found, but one metal and one proton. The only other system that can be compared with ours is a phenolate anion bridging a Zn^{II} centre and a cationic $BPh_2{}^+$ fragment.[11] Therefore, the second amino substituent plays an active role in the complexation process, not by directly coordinating to Zn, but by trapping the H^+ ion of deprotonated phenol and producing an ammonium salt, the resulting zwitterionic compound being stabilised by intramolecular hydrogen bonding.

Acknowledgements

We acknowledge financial support from the French Ministère de l'Education Nationale, de la Recherche et de la Technologie and from the Natural Sciences and Engineering Research Council of Canada.

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Received in Montpellier, France, 24th December 1997;
Revised m/s received 4th *May* 1998; *Paper* 8/00526E