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Alcohol adducts of zinc dichloride: Molecular structure of $[ZnCl_2(THF)\{1\text{-}HOC(C_6H_{11})_2\text{-}2\text{-}NMe_2C_6H_4\}]$

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ABSTRACT

The aminoalcohols $1\text{-}HOCR_2\text{-}2\text{-}NMe_2C_6H_4$ [R = Ph (**1**), R = C_6H_{11} (**2**)] and $1\text{-}HOCPh_2CH_2\text{-}2\text{-}NMe_2C_6H_4$ (**3**) react with $ZnCl_2$ in tetrahydrofuran to give the alcohol adducts $[ZnCl_2(THF)\{1\text{-}HOCR_2\text{-}2\text{-}NMe_2C_6H_4\}]$ [R = Ph (**4**), R = C_6H_{11} (**5**)] and $[ZnCl_2(THF)\{1\text{-}HOCPh_2CH_2\text{-}2\text{-}NMe_2C_6H_4\}]$ (**6**). The complexes **4**–**6** were characterized by ^1H and ^{13}C NMR spectroscopy, and **5** was also structurally characterized by X-ray crystallography.

1. Introduction

The importance of zinc in bioinorganic chemistry [1] has prompted us to extend our studies on the synthesis and solid-state structures of chelated *N,O* and *N,N* complexes [2] to zinc derivatives. Zinc is a constituent and activator of over 150 different enzymes of metabolic pathways; e.g., it is present in the active site in hydrolytic enzymes, where it is coordinated by hard donor atoms (N or O) [3,4], and it is a constituent of the hormone insulin [5]. There is a considerable number of zinc complexes with *N,O* chelate ligands containing the *O* donor as an alkoxide function [6]. *N,O* chelation modes including both *N* and *O* as donor atoms have been reported as well [7], also for macrocyclic Schiff base zinc complexes [8]. *O,O′* Bidentate chelation was observed in heterobi- and heterotrimetallic complexes containing zinc, copper and cobalt [9]. However, there are only a few examples of zinc complexes containing neutral alcohols as ligands [10]. We now report the high-yield synthesis and spectroscopic properties of zinc complexes which contain neutral *O*-coordinating non-chelating dimethylamino alcohol ligands $[ZnCl_2(THF)\{1\text{-}HOCR_2\text{-}2\text{-}NMe_2C_6H_4\}]$ [R = Ph (**4**), R = C_6H_{11} (**5**)] and $[ZnCl_2(THF)\{1\text{-}HOCPh_2CH_2\text{-}2\text{-}NMe_2C_6H_4\}]$ (**6**) and the crystal structure of complex **5**.

2. Synthesis and spectroscopic properties

The colorless zinc complexes **4**–**6** can be readily prepared by addition of $ZnCl_2$ to equimolar amounts of the organic ligands **1** [11,12], **2** [12] or **3** [12,13] in tetrahydrofuran at room temperature (Scheme 1). In the ^1H NMR spectra, the most noticeable signal is that due to the $N(CH_3)_2$ and OH protons, which give rise to singlets at about 3.44 ppm and 9.75 ppm (**4**), 3.38 ppm and 10.31 ppm (**5**), and 2.49 ppm and 7.14 ppm (**6**), respectively. The signals of the methylene protons in **6** are observed at 3.73 ppm. The $^{13}C\{^1H\}$ NMR spectra show singlets for the $N(CH_3)_2$ and CO carbon atoms at 45.1 ppm and 82.3 ppm (**4**), 46.4 ppm and 83.2 ppm (**5**), and 45.0 ppm and 77.0 ppm (**6**). The signal of the methylene carbon atom in **6** is observed at 44.7 ppm. The signals corresponding to the cyclohexyl and the aromatic carbons show the characteristic resonances in their expected chemical shift regions similar to that observed for the organic ligands **1**–**3** [12]. The EI mass spectra only showed the ion peaks for the organic ligands **1**–**3**.

2.1. Molecular structure of $[ZnCl_2(THF)\{1\text{-}HOCCy_2\text{-}2\text{-}NMe_2C_6H_4\}]$ (5)

Colorless crystals of **5** were obtained from tetrahydrofuran at 20 °C. Compound **5** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **5** shows a distorted tetrahedral environment of zinc by two chloro ligands and two neutral *O*-donor molecules (Fig. 1) with bond angles far from the value of 109.47° typical for an ideal tetrahedron. The Cl(1)–Zn–Cl(2) [122.62(4)°] and O(1)–Zn–Cl(1) [123.44(4)°] angles are large, while the four other angles are small [98.91(4)–104.1(4)°] (Table 1).

The dative Zn–O bond [14] of the Zn–O(THF) group [av. 2.058(2) Å] is in the same range of those in $[ZnCl_3(THF)]^-$ [2.025(3)–2.121(8) Å] [15] and in $[Zn(2,4,6\text{-}{}^tBu_3C_6H_2)_2(THF)_2]$ [av. 2.077 Å] [16]. The Zn–O(alcohol) bond length of 1.973(1) Å is slightly smaller and comparable to those in $[Zn(SC_6F_6)_2(3\text{-}$

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$$\text{1-HOCR}_2\text{-2-NMe}_2\text{C}_6\text{H}_4 \xrightarrow{\text{ZnCl}_2} [\text{ZnCl}_2(\text{THF})\{\text{1-HOCR}_2\text{-2-NMe}_2\text{C}_6\text{H}_4\}]$$

$$[\text{R} = \text{Ph}\ (\mathbf{4}),\ \text{R} = \text{C}_6\text{H}_{11}\ (\mathbf{5})]$$

$$\text{1-HOCPh}_2\text{CH}_2\text{-2-NMe}_2\text{C}_6\text{H}_4 \xrightarrow{\text{ZnCl}_2} [\text{ZnCl}_2(\text{THF})\{\text{1-HOCPh}_2\text{CH}_2\text{-2-NMe}_2\text{C}_6\text{H}_4\}]\ (\mathbf{6})$$

Scheme 1. Preparation of **4**–**6**.

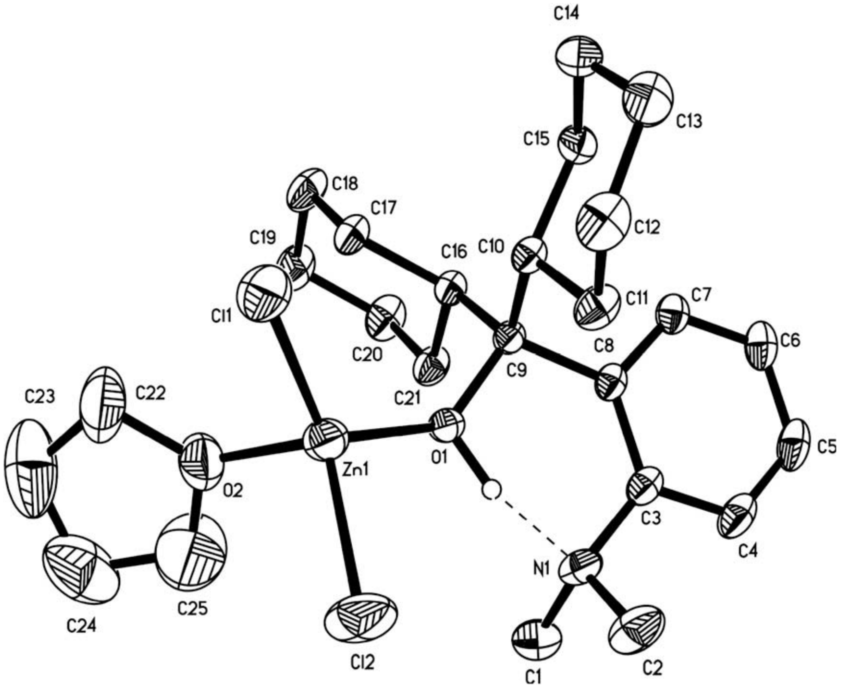


Fig. 1. Molecular structure of **5** showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL-PLUS; XP) [18]. Hydrogen atoms (other than O–H) are omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for **5**.

Zn(1)–O(1)	1.973(1)	O(1)–Zn(1)–Cl(1)	123.44(4)
Zn(1)–O(THF)$_{av.}$	2.058(2)	O(THF)–Zn(1)–Cl(1)$_{av.}$	102.3(3)
Zn(1)–Cl(1)	2.1949(6)	O(1)–Zn(1)–Cl(2)	98.91(4)
Zn(1)–Cl(2)	2.2092(7)	O(THF)–Zn(1)–Cl(2)$_{av.}$	104.1(4)
Cl(1)–Zn(1)–Cl(2)	122.62(4)	O(1)–Zn(1)–O(THF)$_{av.}$	102.6(6)

$(CH_2OH)C_5H_4N)$] [2.123(3) Å], and similar to those found in {*N,N'*-bis[1-(2-hydroxy-4-methoxyphenyl)ethylidene]ethylenediamine-κ^2*O,O'*}dichlorozinc(II) [1.975(5) Å] [7]. The Zn–Cl bond lengths (Table 1) are in the same range and comparable to those found in [$ZnCl_2(C_{10}H_{12}NO_2)_2$] [2.219(2)–2.233(2) Å] [7] and [$ZnCl_2$(8-(diphenylphosphino)quinoline] [2.218(2) and 2.201(2) Å] [17].

The non-involvement of the NMe_2 nitrogen atom in zinc coordination seems to be due to two combined factors: the better donor quality of the THF molecule, and the strong intramolecular O(1)–H(9)···N(1) hydrogen bond [O–H 0.94(3) Å, H···N 1.55(3) Å, O···N 2.464(2) Å, O–H–N 160(3)°]. The intramolecular O(1)–H(9)···N(1) hydrogen bond of **5** is stronger than that in the free ligand **2** [O–H 0.92(2) Å, N···H 1.73(2) Å, N···O 2.591(1) Å, N–H···O 155(2)°] [12]. The bond lengths and angles of the organic fragment of **5** are similar to those observed for the corresponding free ligand **2** [12].

3. Experimental

All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under nitrogen [19]. The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker). Chemical shifts for ^1H and ^{13}C NMR spectra are reported in parts per million (ppm) at 400.13 MHz and 100.63 MHz with tetramethylsilane as external standard. Elemental analyses were determined with a VARIO EL (Heraeus). Melting points (Gallenkamp) are uncorrected. Mass spectra were recorded with an MAT-8230 (EI-MS, 70 eV). 1-$HOCPh_2$-2-$NMe_2C_6H_4$ (**1**) [11,12], 1-$HOC(C_6H_{11})_2$-2-$NMe_2C_6H_4$ (**2**) [12], and 1-$HOCPh_2CH_2$-2-$NMe_2C_6H_4$ (**3**) [12,13] were prepared by literature procedures.

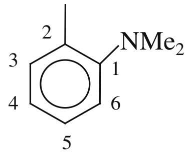
3.1. Preparation of [$ZnCl_2$(THF){1-$HOCPh_2$-2-$NMe_2C_6H_4$}] (4)

A 150 ml Schlenk flask was charged with 1-$HOCPh_2$-2-$NMe_2C_6H_4$ (**1**) (0.48 g, 1.6 mmol) and tetrahydrofuran (50 ml). Then $ZnCl_2$ (0.22 g, 1.6 mmol) was added at room temperature. The solution was stirred for about 3 h. The remaining solid was then removed by filtration and the solution was concentrated to give the product in 94% yield. Mp. 177–178 °C. ^1H NMR (DMSO, δ/ppm): 1.76 (m, 4H, CH_2 (THF)), 3.44 (s, 6H, $N(CH_3)_2$), 3.60 (m, 4H, CH_2O (THF)), 6.56–7.54 (m, vbr, 14H, C_6H_4 and C_6H_5), 9.75 (s, 1H, OH). ^{13}C {^1H} NMR (DMSO, δ/ppm): 21.0 (THF), 45.1 ($N(CH_3)_2$), 67.0 (THF), 82.3 (C–O), 124.3 (s, C6 in C_6H_4), 125.2 (s, C4 in C_6H_4), 126.9 (s, C3 in C_6H_4), 127.8 (s, C5 in C_6H_4), 128.6 (s, *p*-C in C_6H_5), 129.5 (s, *o*-C in C_6H_5), 139.0 (s, *m*-C in C_6H_5), 142.3 (s, C2 in C_6H_4), 147.5 (s, C1 in C_6H_4), 152.0 (s, *ipso*-C in C_6H_5). MS: *m/z* 303.4 (M^+-$ZnCl_2$-THF). Found: C, 58.64; H, 5.69; N, 2.72%. Calcd. for $C_{25}H_{29}Cl_2NO_2Zn$ (511.80): C, 58.67; H, 5.71; N, 2.74%.

Table 2
Crystal data and structure refinement for **5**.

Formula	$C_{25}H_{41}Cl_2NO_2Zn$	Z	2
Formula weight	523.86	D_{calcd} (g cm^{-1})	1.316
Temperature (K)	298(2)	$F(0\,0\,0)$	556
Crystal system	Triclinic	Crystal size (mm)	0.60 × 0.50 × 0.40
Space group	$P\bar{1}$	Absorption coefficient (mm^{-1})	1.152
a (Å)	8.9841(7)	Number of reflections collected	12485
b (Å)	9.5300(7)	Number of independent reflections	6197
c (Å)	16.838(1)	R_{int}	0.0231
α (°)	81.206(2)	Number of parameters	459
β (°)	85.350(1)	R_1 ($I > 2\sigma(I)$)	0.0381
γ (°)	68.180(1)	wR_2 (all data)	0.1136
V (Å^3)	1322.1(2)	$(\Delta/\rho)_{min}$ (e Å^{-3})	0.497
Deposition number	194 393	$(\Delta/\rho)_{max}$ (e Å^{-3})	−0.406

Phenylene ring numbering scheme:



3.2. Preparation of [ZnCl$_2$(THF){1-HOCCy$_2$-2-NMe$_2$C$_6$H$_4$}] (**5**)

A similar procedure to that described for **4** was used here, except 1-HOC(C_6H_{11})$_2$-2-NMe$_2$C$_6$H$_4$ (**2**) (0.51, 1.6 mmol) was employed instead of **1** and colorless crystals were obtained from tetrahydrofuran at 20 °C in 80% yield. Mp. 170–172 °C. ^{1}H NMR (DMSO, δ/ppm): 0.69–1.73 (vbr, 22H, C_6H_{11}), 1.77 (m, 4H, CH_2 (THF)), 3.38 (s, 6H, N(CH_3)$_2$), 3.61 (m, 4H, CH_2O (THF)), 10.31 (s, 1H, OH), 7.04–7.39 (m, 4H, C_6H_4). ^{13}C {^{1}H} NMR (DMSO, δ/ppm): 21.0 (THF), 26.4 (s, C4 in C_6H_{11}), 29.2 (s, C3/C5 in C_6H_{11}), 30.4 (s, C2/C6 in C_6H_{11}), 45.8 (s, C1 in C_6H_{11}), 46.4 (N(CH_3)$_2$), 67.0 (THF), 83.2 (C–O), 124.5 (s, C6 in C_6H_4), 125.4 (s, C4 in C_6H_4), 126.1 (s, C3 in C_6H_4), 127.3 (s, C5 in C_6H_4), 137.8 (s, C2 in C_6H_4), 153.3 (s, C1 in C_6H_4). MS: *m/z* 315.6 (M$^+$-ZnCl$_2$-THF). Found: C, 57.10; H, 7.87; N, 2.66%. Calcd. for $C_{25}H_{41}Cl_2NO_2Zn$ (523.89): C, 57.32; H, 7.89; N, 2.67%.

3.3. Preparation of [ZnCl$_2$(THF){1-HOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$}] (**6**)

A similar procedure to that described for **4** was used here, except 1-HOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$ (**3**) (0.51, 1.6 mmol) was employed instead of **1** and the product was obtained from tetrahydrofuran at 20 °C in 80% yield. Mp. 190–192 °C. ^{1}H NMR (DMSO, δ/ppm): 1.77 (m, 4H, CH_2 (THF)), 2.49 (s, 6H, N(CH_3)$_2$), 3.61 (m, 4H, CH_2O (THF)), 3.73 (s, 2H, CH_2), 7.14 (s, 1H, OH), 7.16–7.45 (m, vbr, 14H, C_6H_4 and C_6H_5). ^{13}C {^{1}H} NMR (DMSO, δ/ppm): 21.0 (THF), 44.7 (CH_2), 45.0 (N(CH_3)$_2$), 67.0 (THF), 77.0 (C–O), 124.5 (s, C6 in C_6H_4), 125.4 (s, C4 in C_6H_4), 126.1 (s, C3 in C_6H_4), 127.6 (s, C5 in C_6H_4), 128.4 (s, *p*-C in C_6H_5), 130.0 (s, *m*-C in C_6H_5), 130.9 (s, *o*-C in C_6H_5), 142.0 (s, C2 in C_6H_4), 148.0 (s, C1 in C_6H_4), 152.3 (s, *ipso*-C in C_6H_5). MS: *m/z* 317.3 (M$^+$-ZnCl$_2$-THF). Found: C, 59.37; H, 5.94; N, 2.65%. Calcd. for $C_{26}H_{31}Cl_2NO_2Zn$ (525.83): C, 59.39; H, 5.94; N, 2.66%.

3.4. Data collection and structure refinement of **5**

Crystallographic data are given in Table 2. Data [λ(Mo Kα) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction was performed with SADABS [20]. The structure was solved by direct methods (SHELXTL-PLUS [15]). H atoms were located by difference maps and refined isotropically, except for the hydrogen atoms of the disordered THF ligand (O2, C22–C25 and O3, C26–C29; these atoms were refined with 63% and 37% occupancy, respectively).

Appendix A. Supplementary data

CCDC 194393 contains the supplementary crystallographic data for **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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