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Unique formation of mono-, tetra- and nona-nuclear zinc complexes from protonolysis reactions of $[Zn(dmpzm)Et_2]$†

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Protonolysis reactions of $[Zn(dmpzm)Et_2]$ (**1**) with acetic or formic acid in different molar ratios gave rise to four mononuclear zinc complexes [ZnEt(dmpzm)(L)] (**2**: L = OAc; **3**: L = HCOO) and $[Zn(dmpzm)(L)_2]$ (**4**: L = OAc; **5**: L = HCOO), one nonanuclear zinc complex $[Zn(\mu_4\text{-}O)_2(ZnEt)_6(\mu_3\text{-}OAc)_4(\mu'_3\text{-}OAc)_2\{Zn(dmpzm)Et\}_2]$ (**6**), and one tetranuclear zinc complex $[Zn_4(\mu_4\text{-}O)(dmpzm)_3Et_3]$ (**7**). Compounds **1–7** were characterized by elemental analysis, IR spectra, ^1H NMR spectra, and the crystal structures of **1**, **3**, **4**, **6**, and **7** were determined by single-crystal X-ray crystallography. In the structures of **1**, **3**, and **4**, the central Zn atom is tetrahedrally coordinated by two N atoms of one dmpzm and two C atoms of two Et groups (**1**), or one C atom of one Et group and one O atom of formate ligand (**3**), or two O atoms of two acetates (**4**). In the structure of **6**, a heptanuclear $[Zn(\mu_4\text{-}O)_2(ZnEt)_6(\mu_3\text{-}OAc)_4]$ core is connected with two $[Zn(dmpzm)Et]^+$ fragments *via* a pair of μ'_3-OAc ligands. Compound **7** consists of a $Zn_4(\mu_4\text{-}O)$ tetrahedron in which three Zn atoms are further saturated by two N atoms from dmpzm ligands and an ethyl group while one Zn center is coordinated by three C atoms from the methylene group of the three dmpzm ligands.

Introduction

Alkylzinc compounds are found to be of importance in catalysis, organic synthesis, and materials.[1] Some alkylzinc compounds have been employed to react with donor ligands to form various mononuclear adducts and polynuclear zinc complexes.[2–4] Among the mononuclear Zn adducts, those containing N-donor ligands are useful precursors to form other interesting zinc complexes.[3,4] Some of them were used as model complexes to mimic the structures or functions of the active site of zinc enzymes[3] or as special catalysts for the ring-opening polymerization of *rac*-lactide,[4a,g] and for the copolymerization of carbon oxide and epoxides.[1b,4b] Currently, most of the mononuclear adducts are engaged in the utilization of the 3 N tripodal ligands such as hydridotris(pyrazol-1-yl)borate and some mixed ligands that incorporate histidine-like nitrogens and one or more thioether, thiolate, aldehyde, methoxy, carboxyl and phenolate donor atoms. Their reactivity towards H_2O, ROH, and RCOOH have been extensively investigated.[3,4g] Although the mononuclear adducts of the 2 N bipodal ligands have also been described,[5] studies on the reactivity of those of the neutral 2 N bipodal ligands are less explored.[1b,4c] In this context, we deliberately chose diethylzinc ($ZnEt_2$) to react with a neutral 2 N bipodal ligand bis(3,5-dimethylpyrazolyl)methane (dmpzm)[6] and isolated their adduct $[Zn(dmpzm)Et_2]$ (**1**). Complex **1** has two terminal ethyl groups that may be protonated by carboxylic acids to form ethane molecules. The resulting mononuclear zinc complexes with a possible N_2O_2 coordination sphere may resemble those found in the active sites of thermolysin or carboxypeptidase.[3a,b,7] To this end, we carried out reactions of **1** with acetic and formic acids to prepare our expected zinc model complexes. However, such reactions were complicated and four mononuclear zinc complexes [ZnEt(dmpzm)(L)] (**2**: L = OAc; **3**: L = HCOO) and $[Zn(dmpzm)(L)_2]$ (**4**: L = OAc; **5**: L = HCOO) along with one unusual nonanuclear zinc complex $[Zn(\mu_4\text{-}O)_2(ZnEt)_6(\mu_3\text{-}OAc)_4(\mu'_3\text{-}OAc)_2\{Zn(dmpzm)Et\}_2]$ (**6**) and one tetranuclear zinc complex $[Zn_4(\mu_4\text{-}O)(dmpzm)_3Et_3]$ (**7**) were isolated. We herein report the intriguing reactivity of **1** towards the two acids along with the isolation and structural characterization of **1–7**.

Experimental

Materials and methods

All manipulations were carried out under high purity nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over sodium-benzophenone (THF, toluene, and *n*-hexane), P_2O_5 (MeCN) and freshly distilled prior to use. The ligand bis(3,5-dimethylpyrazol-1-yl)methane (dmpzm) was prepared according to the literature method.[6] Other chemicals and reagents were obtained from commercial sources and used as received. ^1H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. ^1H NMR chemical shifts were referenced to the solvent signal in C_6D_6. Elemental analyses for C, H, and N were performed on a Carlo-Erbo CHNO–S microanalyzer. The IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000–400 cm^{-1}).

Synthesis of $[Zn(dmpzm)Et_2]$ (1). To a solution of $ZnEt_2$ (3.0 mL of a 1M solution in hexane, 3.0 mmol) in THF (10 mL) was

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added a solution of dmpzm (0.61 g, 3 mmol) in THF (10 mL). The colorless solution was stirred at ambient temperature for 5 h, and was concentrated to *ca.* 5 mL. Colorless crystals of **1** were isolated by cooling the solution to –26 °C for 2 days. Yield: 0.75 g (76%). Anal. Calcd. for $C_{15}H_{26}N_4Zn$: C, 54.96; H, 7.80; N, 17.09; Found: C, 54.58; H, 7.65; N, 17.43%. IR (KBr disk): 2977 (m), 2924 (m), 1558 (s), 1486 (s), 1471 (m), 1464 (m), 1456 (m), 1417 (m), 1384 (s), 1353 (s), 1313 (m), 1267 (s), 1139 (m), 1084 (m), 1035 (m), 970 (w), 809 (s), 783 (m), 712 (m), 673 (s), 627 (s) cm^{-1}. ^1H NMR (400 MHz, ppm): (C_6D_6) δ –5.457 (s, 2H, -CH), 5.372(s, 2H, $-CH_2$), 2.240 (s, 6H, $-CH_3$), 1.675 (s, 6H, $-CH_3$), 1.565 (t, $^3J = 8.0$ Hz, 6H, $-ZnCH_2CH_3$), 0.636 (q, $^3J = 12.4$ Hz, 4H, $-ZnCH_2CH_3$).

Synthesis of [ZnEt(dmpzm)(OAc)] (2). To a solution of **1** (0.62 g, 1.90 mmol) in 15 mL toluene was added a solution of HOAc (0.11 mL, 1.90 mmol) at room temperature. After the evolution of gas ceased, the mixture was stirred overnight and then filtered. *n*-Hexane (15 mL) was allowed to diffuse into the filtrate. Then the white solid of **2** were formed, which were collected by filtration, washed by dry hexane and dried in vacuo. Yield: 0.59 g (87%). Anal. Calcd. for $C_{15}H_{24}N_4O_2Zn$: C, 50.36; H, 6.76; N, 15.66; Found: C, 49.69; H, 6.65; N, 15.17%. IR (KBr disk): 3138 (w), 3019 (w), 2962 (w), 2947 (m), 2926 (m), 2890 (s), 2844 (s), 1615 (s), 1579 (s), 1558 (s), 1468 (m), 1445 (s), 1421 (s), 1375 (s), 1322(s), 1286 (s), 1235 (m), 1044 (m), 1004 (m), 973 (w), 920 (w), 810 (s), 706 (w), 678 (s), 600 (m), 510 (m) cm^{-1}. ^1H NMR (400 MHz, ppm): (C_6D_6) δ –5.763(s, 2H, -CH), 5.484(s, 2H, $-CH_2$), 2.238 (s, 6H, $-CH_3$), 2.156 (s, 6H, $-CH_3$), 1.934 (s, 3H $-CH_3COO$), 1.752 (t, $^3J = 8.2$ Hz, 3H, $-ZnCH_2CH_3$), 0.780 (q, $^3J = 10.0$ Hz, 2H, $-ZnCH_2CH_3$).

Synthesis of [ZnEt(dmpzm)(HCOO)] (3). Compound **3** (0.47 g, 83%) was isolated as colorless crystals from the reaction of **1** (0.54 g, 1.66 mmol) with HCOOH (62.9 µL, 1.66 mmol) in 10 mL toluene and 10 mL CH_3CN followed by a similar workup to that used in the isolation of **2**. Anal. Calcd. for $C_{14}H_{22}N_4O_2Zn$: C, 48.92; H, 6.45; N, 16.30; Found: C, 49.29; H, 6.64; N, 15.93%. IR (KBr disk): 3132 (w), 3005 (m), 2927 (m), 2903 (m), 2851 (m), 2797 (m), 2720 (m), 2687 (w), 1626 (s), 1593 (s), 1557 (s), 1467 (m), 1425 (s), 1391 (m), 1383 (m), 1312(s), 1286 (s), 1233 (m), 1160 (w), 1150 (w), 1116 (w), 1048 (s), 1005 (w), 985 (w), 922 (w), 828 (m), 812 (m), 780 (s), 703 (m), 679 (s), 630 (m), 601 (s), 506 (m) cm^{-1}. ^1H NMR (400 MHz, ppm): (C_6D_6) δ –8.426 (br, 1H, -HCOO), 5.867 (s, 2H, -CH), 5.507(s, 2H, $-CH_2$), 2.196 (s, 6H, $-CH_3$), 2.136 (s, 6H, $-CH_3$), 1.777 (t, $^3J = 8.4$ Hz, 3H, $-ZnCH_2CH_3$), 0.797 (q, $^3J = 10.0$ Hz, 2H, $-ZnCH_2CH_3$).

Synthesis of [Zn(dmpzm)(OAc)$_2$](4). To a solution of **1** (0.69 g, 2.10 mmol) in 25 mL toluene was added HOAc (0.25 mL, 4.20 mmol) at room temperature. Gas evolution was observed. The solution was stirred at ambient temperature for 40 min. After this time, the evolution of gas ceased, and the reaction mixture was further stirred overnight at room temperature and then filtered. The filtrate was kept at ambient temperature for one week to form colorless crystals of **4**. Yield: 0.68 g (83%). Anal. Calcd. for $C_{15}H_{22}N_4O_4Zn$: C, 46.46; H, 5.72; N, 14.45; Found: C, 46.53; H, 6.05; N, 14.37%. IR (KBr disk): 3129 (w), 3014 (w), 2968 (w), 2937 (m), 2919 (m), 2894 (s), 2837 (s), 1585 (s), 1560 (s), 1463 (m), 1439 (s), 1410 (s), 1390 (s), 1338(m), 1285 (m), 1049 (w), 1018 (w), 967 (w), 923 (w), 829 (m), 682 (s), 627 (m), 479 (w) cm^{-1}. ^1H NMR (400 MHz, ppm): (C_6D_6) δ –5.601(s, 2H, -CH), 5.554(s, 2H, $-CH_2$), 2.254 (s, 6H, $-CH_3$), 2.152 (s, 6H, $-CH_3$), 1.905 (s, 6H $-CH_3COO$).

Synthesis of [Zn(dmpzm)(HCOO)$_2$] (5). To a solution of **1** (0.66 g, 2.20 mmol) in 20 mL toluene was added HCOOH (0.17 mL, 4.40 mmol) at room temperature. After the evolution of gas ceased, some insoluble white precipitate was formed. The resulting solution was further stirred overnight at room temperature and then filtered. *n*-Hexane (15 mL) was allowed to diffuse into the filtrate. Then the white solid of Zn(dmpzm)(HCOO)$_2$ (**5**) was formed, which were collected by filtration, washed by absolute hexane and dried *in vacuo*. Yield: 0.53 g (67%). Anal. Calcd. for $C_{13}H_{18}N_4O_4Zn$: C, 43.41; H, 5.04; N, 15.58; Found: C, 43.19; H, 5.45; N, 15.47%. IR (KBr disk): 3133 (w), 3012 (w), 2942 (w), 2926 (m), 2895 (s), 2834 (s), 2752 (m), 2692 (w), 1629 (s), 1589 (s), 1558 (s), 1469 (m), 1435 (s), 1421 (s), 1384 (s), 1318 (s), 1286 (s), 1233 (m), 1044 (m), 1007 (m), 978 (w), 921 (w), 808 (s), 705 (w), 678 (s), 600 (m), 510 (m) cm^{-1}. ^1H NMR (400 MHz, ppm): (C_6D_6) δ –8.413 (br, 2H, -HCOO), 5.787 (s, 2H, -CH), 5.614 (s, 2H, $-CH_2$), 2.217 (s, 6H, $-CH_3$), 2.139 (s, 6H, $-CH_3$).

Synthesis of [Zn(µ$_4$-O)$_2$(ZnEt)$_6$(µ$_3$-OAc)$_4$(µ′$_3$-OAc)$_2${Zn-(dmpzm)Et}$_2$]·2C$_7$H$_8$ (6·2C$_7$H$_8$). To a solution of **1** (0.93 g, 2.84 mmol) in 15 mL toluene was added HOAc (81.8 µL, 1.42 mmol) at room temperature. Gas evolution was observed. The solution was stirred at ambient temperature for 30 min. After this time, gas evolution had ceased, the reaction mixture was further stirred overnight at room temperature. Then the solution was reduced *in vacuo* to 8 mL. Colorless crystals of **6**·2C$_7$H$_8$ was formed by cooling the solution to –26 °C for 1 month. Yield: 0.081 g (17%). Anal. Calcd. for $C_{64}H_{106}N_8O_{14}Zn_9$: C, 42.70; H, 5.94; N, 6.22; Found: C, 42.56; H, 6.01; N, 6.43%. IR (KBr disk): 3137 (m), 3015 (m), 2979 (m), 2925 (s), 2891 (s), 2844 (s), 1614 (s), 1579 (s), 1557 (s), 1464 (s), 1383 (s), 1353 (s), 1322(s), 1286 (s), 1268 (s), 1235 (m), 1139 (m), 1043 (s), 1005 (s), 985 (m), 971 (m), 953 (m), 920 (m), 827 (m), 810 (s), 783 (s), 776 (m), 673 (s), 628 (s), 614 (m), 600 (m), 509 (m), 470 (m) cm^{-1}. ^1H NMR (400 MHz, ppm): (C_6D_6) δ –5.863(s, 4H, -CH), 5.435(s, 4H, $-CH_2$), 2.138 (s, 12H, $-CH_3$), 2.106 (s, 12H, $-CH_3$), 2.011 (s, 18H $-CH_3COO$), 1.821 (t, $^3J = 8.0$ Hz, 18H, $-ZnCH_2CH_3$), 1.731 (t, $^3J = 12.0$ Hz, 6H, $-ZnCH_2CH_3$), 0.901 (q, $^3J = 10.0$ Hz, 12H, $-ZnCH_2CH_3$), 0.720 (q, $^3J = 8.0$ Hz, 4H, $-ZnCH_2CH_3$). On the other hand, white solid of **2** was obtained by slowly diffusing *n*-hexane (10 ml) into the toluene solution, which were collected by filtration, washed twice with absolute *n*-hexane and dried *in vacuo.* Yield: 0.19 g (39%).

Synthesis of [Zn$_4$(dmpzm)$_3$Et$_3$(µ$_4$-O)] (7).

Method 1. To a solution of 1 (0.85 g, 2.60 mmol) in 10 mL toluene was added HCOOH (49.3 µL, 1.30 mmol) at room temperature. After the evolution of gas ceased, some insoluble white precipitate was formed. The resulting solution was further stirred overnight at room temperature and then filtered. The filtrate was kept at –26 °C for one month to form colorless crystals of **7**. Yield: 0.15 g (20%). Anal. Calcd. for $C_{39}H_{60}N_{12}OZn_4$: C, 48.06; H, 6.20; N, 17.25; Found: C, 47.89; H, 6.53; N, 17.44%. IR (KBr disc): 2945(w), 2923 (m), 2880 (w), 2838 (m), 1555 (s), 1459 (m), 1418 (s), 1384 (s), 1353 (m), 1314(w), 1267 (s), 1211 (w), 1140 (w), 1041 (m), 1033 (m), 971 (w), 922 (w), 844 (w), 805 (m), 776 (s), 713 (w), 673 (s), 628 (w), 587 (m), 470 (s) cm^{-1}. ^1H NMR

Table 1 Crystal data and structure refinement parameters for complexes **1**, **3**, **4**, **6**·$2C_7H_8$ and **7**

Compounds	**1**	**3**	**4**	**6**·$2C_7H_8$	**7**
Formula	$C_{15}H_{26}N_4Zn$	$C_{14}H_{22}N_4O_2Zn$	$C_{15}H_{22}N_4O_4Zn$	$C_{64}H_{106}N_8O_{14}Zn_9$	$C_{39}H_{60}N_{12}OZn_4$
Formula weight	327.77	343.73	387.74	1800.08	974.47
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Cubic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/m$	$P2_13$
a/Å	8.3359(17)	7.8314(16)	13.681(3)	23.993(5)	16.5114(19)
b/Å	14.195(3)	10.326(2)	8.2077(16)	13.776(3)	16.5114(19)
c/Å	14.467(3)	11.652(2)	15.815(3)	15.394(3)	16.5114(19)
α/°		106.46(3)			
β/°	103.53(3)	106.65(3)	97.97	128.64(3)	
γ/°		102.01(3)			
V/Å^3	1664.4(6)	821.7(3)	1758.7(6)	3974(2)	4501.4(9)
T/K	193	193	193	193	193
Z	4	2	4	2	4
D_c/g cm^{-3}	1.308	1.389	1.464	1.504	1.438
F(000)	696	360	808	1856	2024
μ(Mo Kα)/mm^{-1}	1.473	1.504	1.423	2.725	2.150
Total reflections	15690	8100	16535	19491	44810
Unique reflections	3023 (R_{int} = 0.0427)	2983 (R_{int} = 0.0396)	3215 (R_{int} = 0.0349)	3781 (R_{int} = 0.0605)	2757 (R_{int} = 0.1013)
No. of observations	2451	2455	2832	3082	2654
No. of parameters	187	195	211	232	175
Flack parameters					0.42(4)
R^a	0.038	0.0557	0.0656	0.064	0.0449
wR^b	0.107	0.1144	0.1644	0.1308	0.0986
GOF^c	1.062	1.097	1.116	1.139	1.071

[a] $R = \sum\|F_o| - |F_c|/\sum|F_o|$. [b] $wR = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [c] $GOF = \{\sum[w((F_o^2 - F_c^2)^2)/(n - p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

(400 MHz, ppm): (C6D6) δ –5.587 (s, 6H, -CH), 5.568(s, 3H, -CH), 2.277 (s, 18H, -CH_3), 2.1149 (s, 18H, -CH_3), 1.790 (t, ^3J = 8.0 Hz, 9H, -$ZnCH_2CH_3$), 0.799 (q, ^3J = 8.2 Hz, 6H, -$ZnCH_2CH_3$). On the other hand, the white solid was re-dissolved in MeCN (10 ml) to give a colorless solution. Colorless crystals of **3** were isolated by cooling the solution to –26 °C for one week. Yield: 0.26 g (35%).

Method 2. To a solution of **1** (0.88 g, 2.68 mmol) in 15 mL toluene was added a solution of H_2O (0.67 mmol) in THF (0.13 mL) at room temperature. After the evolution of gas ceased, the mixture was stirred overnight and then filtered. The filtrate was kept at room temperature for 3 days to form colorless crystals of **7**. Yield: 0.57 g (87%).

X-Ray crystallography

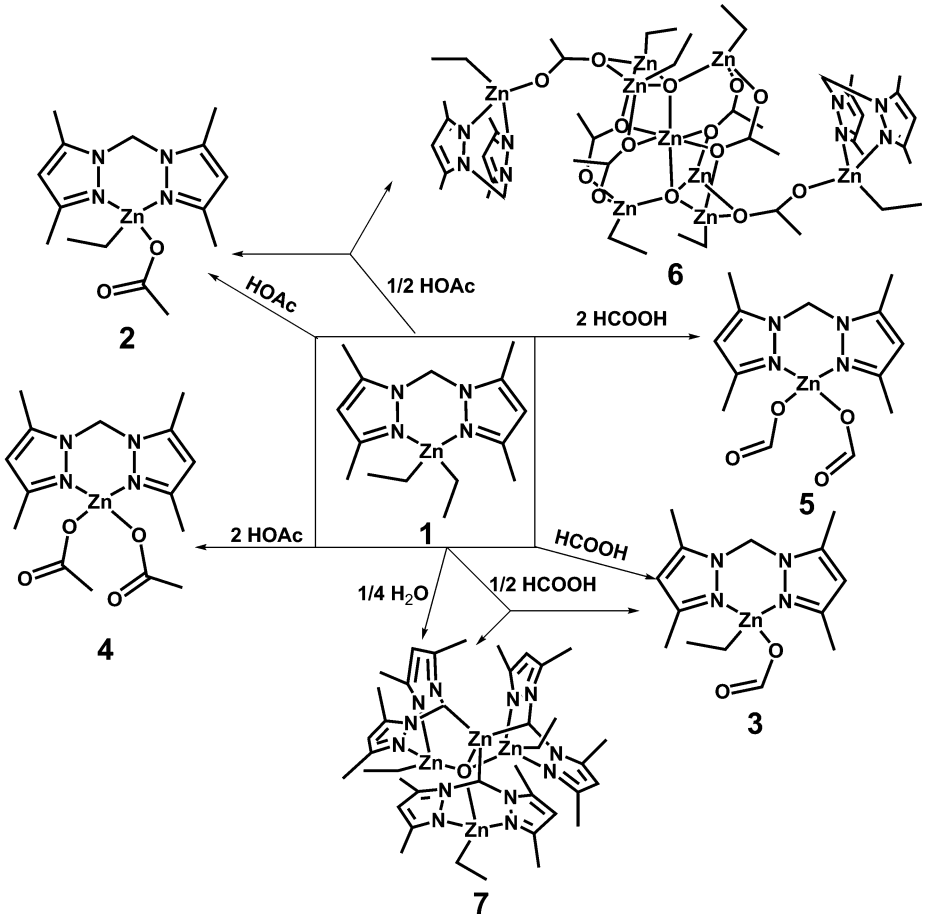
All measurements were made on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) at 193 K by using graphite monochromated Mo Kα (λ = 0.71073 Å). Single crystals of **1**, **3**, **4**, **6**·$2C_7H_8$ and **7** were obtained directly from the above preparations. A colorless chunk of **1** with dimensions 0.55 × 0.50 × 0.30 mm, a colorless chunk of **3** with dimensions 0.60 × 0.20 × 0.15 mm, a colorless prism of **4** with dimensions 0.40 × 0.40 × 0.30 mm, a colorless prism of **6**·$2C_7H_8$ with dimensions 0.36 × 0.20 × 0.18 mm, a colorless prism of **7** with dimensions 0.40 × 0.30 × 0.21 mm were mounted into a glass capillary. Diffraction data were collected at ω mode with a detector distance of 35 mm to the crystals. A total of 720 oscillation images for each were collected in the range 6.40° < 2θ < 50.60° for **1**, 6.82° < 2θ < 50.69° for **3**, 6.01° < 2θ < 50.69° for **4**, and 6.40° < 2θ < 50.69° for **6**·$2C_7H_8$, 6.04° < 2θ < 50.69° for **7**. The collected data were reduced by using the program *CrystalClear* (Rigaku and MSC, Ver. 1.3, 2001), and an absorption correction (multi-scan) was applied, which resulted in transmission factors ranging from 0.452 to 0.643 for **1**, from 0.416 to 0.796 for **3**, from 0.572 to 0.655 for **4**, from 0.410 to 0.612 for **6**·$2C_7H_8$, from 0.466 to 0.631 for **7**. The reflection data were also corrected for Lorentz and polarization effects.

The structures of **1**, **3**, **4**, **6**·$2C_7H_8$, and **7** were solved by direct methods and refined by full matrix least-squares on F^2.[8] In the case of **6**·$2C_7H_8$, one Zn atom and two C atoms from an acetyl group were found to be disordered over two sites with an occupancy factor of 0.48/0.52 for Zn(1)/Zn(1A), C(11)/C(11A) and C(12)/C(12A). Because the single crystal used rapidly lost solvent upon removal from its mother liquor and thus was weakly diffracting, especially at high angles, those from toluene solvent molecule and C(9) in **6**·$2C_7H_8$ were refined isotropically. All other non-H atoms in these five compounds were refined anisotropically. All hydrogen atoms were placed in geometrically idealized positions (C–H = 0.98 Å for methyl groups, C–H = 0.99 Å for methylene groups or C–H = 0.95 Å for phenyl groups) and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C), or 1.5 U_{eq}(C) for methyl groups. All the calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). A summary of the important crystallographic information for **1**, **3**, **4**, **6**·$2C_7H_8$, and **7** are tabulated in Table 1.

Results and discussion

Synthetic and spectral aspects

As shown in Scheme 1, complex **1** was prepared in 76% yield from reactions of the solution of $ZnEt_2$ in hexane with equimolar dmpzm in THF. Treatment of **1** with HOAc in a 1 : 1 or 1 : 2 molar ratio afforded colorless crystals of **2** in 87% yield and **4** in



Scheme 1

83% yield. Under similar conditions the use of HCOOH led to the formation of analogous products **3** (78% yield) and **5** (72% yield). Intriguingly, treatment of a toluene solution of **1** with 1/2 equiv. of HOAc at ambient temperature produced not only colorless crystals of **2** in 39% yield, but also a rare nonanuclear zinc carboxylate oxide complex **6** in 17% yield. The preparation for **6** was reproducible, though its yield was always relatively low. Similarly, reactions of **1** with 1/2 equiv. of HCOOH formed **3** in 35% yield and a tetranuclear carboxylate oxide complex **7** in 20% yield. This complex could also be isolated in 87% yield from the reactions of **1** with 1/4 equiv. of water in toluene/THF.

1, **2**, **3**, **6** and **7** were highly air and moisture sensitive, and were readily soluble in toluene, THF, DME, MeCN, while **4** and **5** were soluble in DME, THF, toluene, and MeCN. Elemental analyses of **1**–**7** were consistent with the formulas. The ^{1}H NMR spectrum of **1** showed the methyl and methylene protons of ethyl groups at δ = 1.565 and 0.636 ppm. Other peaks can be assigned to be those of the dmpzm ligand. In the ^{1}H NMR spectra of **2** and **3**, resonances related to the methyl and methylene protons of the ethyl group were at δ = 1.752/0.780 ppm (**2**) and δ = 1.777/0.797 ppm (**3**). For **2** and **4**, a singlet realted to the OAc group was observed at δ = 1.934 ppm (**2**) and 1.905 ppm (**4**) while a broad singlet at δ = 8.426 ppm (**3**) or 8.133 ppm (**5**) may ascribed to the proton of HCOO$^-$ group. In the ^{1}H NMR spectrum of **6**, two sets of signals (δ = 1.821/0.901 and 1.731/0.720 ppm) were observed due to the two different ethyl groups while one singlet at δ = 2.011 ppm was assigned to be the methyl protons of the OAc group. In the ^{1}H NMR spectrum of **7**, two signals at δ = 1.790 and 0.799 ppm were assigned to be the methyl and methylene protons of the Et group. Besides, the singlet at δ = 5.568 ppm belongs to the deprotonated methylene group of the dmpzm ligands. The identities of **1**, **3**, **4**, **6** and **7** were further confirmed by X-ray analysis.

Crystallography

Crystal structure of 1. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ and the asymmetric unit contains one [Zn(dmpzm)Et$_2$] molecule. The Zn center of **1** is tetrahedrally coordinated by two N atoms from one dmpzm ligand and two C atoms from two Et groups (Fig. 1a). The mean Zn–C bond distance (2.000(3) Å) (Table 2) is close to that in [{η^2-B(3-Bu^{t}pz)$_2$}ZnC(CH$_3$)$_3$] (3-Bu^{t}pz = 3-C$_3$N$_2$Bu^{t}H$_2$, 1.995(7) Å).[4c] The mean Zn–N bond length is 2.267(3) Å, which is comparable to that of the corresponding one of [(tmeda)ZnEt$_2$] (temda = *N*,*N*,*N'*,*N'*-tetramethylenediamine, 2.294(5) Å),[9] and somewhat longer than that in [{η^2-B(3-Bu^{t}pz)$_2$}ZnC(CH$_3$)$_3$] (2.042(5) Å).[4c] The adjacent [Zn(dmpzm)Et$_2$] molecules are stacked in a face-to-face fashion with a separation of 3.651 Å between the centroids of the two pyrazolyl rings, indicating the existence of the significant intermolecular π–π interactions.

Crystal structure of 3. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit of **3** contains one

Table 2 Selected bond distances (Å) and angles (°) for **1**, **3**, **4**, **6**·2C_7H_8 and **7**

Compound **1**			
Zn(1)–C(12)	1.998(4)	Zn(1)–C(14)	2.003(3)
Zn(1)–N(1)	2.263(3)	Zn(1)–N(3)	2.271(3)
C(12)–Zn(1)–C(14)	138.89(15)	C(12)–Zn(1)–N(1)	108.76(13)
C(14)–Zn(1)–N(1)	104.00(12)	C(12)–Zn(1)–N(3)	102.34(15)
C(14)–Zn(1)–N(3)	105.19(12)	N(1)–Zn(1)–N(3)	83.94(10)
Compound **3**			
Zn(1)–C(12)	1.975(5)	Zn(1)–O(1)	1.997(3)
Zn(1)–N(1)	2.098(4)	Zn(1)–N(4)	2.106(3)
C(12)–Zn(1)–O(1)	119.94(18)	C(12)–Zn(1)–N(1)	124.5(2)
O(1)–Zn(1)–N(1)	96.58(13)	C(12)–Zn(1)–N(4)	123.04(19)
O(1)–Zn(1)–N(4)	97.37(13)	N(1)–Zn(1)–N(4)	87.60(13)
Compound **4**			
Zn(1)–O(3)	1.946(5)	Zn(1)–O(1)	1.955(5)
Zn(1)–N(1)	2.081(4)	Zn(1)–N(3)	2.110(4)
O(3)–Zn(1)–O(1)	136.8(2)	O(3)–Zn(1)–N(1)	116.4(2)
O(1)–Zn(1)–N(1)	97.14(17)	O(3)–Zn(1)–N(3)	104.67(18)
O(1)–Zn(1)–N(3)	102.17(19)	N(1)–Zn(1)–N(3)	88.88(15)
Compound **6**·2C_7H_8			
Zn(1)–C(8)	1.956(9)	Zn(1)–O(1)	2.037(5)
Zn(1)–N(1)	2.085(5)	Zn(4A)–C(10)	2.520(10)
Zn(2)–O(3)	1.957(5)	Zn(2)–O(4)	2.178(4)
Zn(3)–O(3)	1.940(4)	Zn(3)–C(14)	1.974(7)
Zn(3)–O(5)	2.089(3)	Zn(4)–C(11)	1.898(15)
Zn(4)–O(3)	2.031(3)	Zn(4)–O(2)	2.199(8)
Zn(4)a–O(3)	1.885(4)	Zn(4A)–C(11A)	1.934(14)
O(3)–Zn(4A)–O(2)[a]	85.6(2)	C(8)–Zn(1)–O(1)	121.5(3)
C(8)–Zn(1)–N(1)[a]	122.40(18)	O(1)–Zn(1)–N(1)[a]	95.67(17)
C(8)–Zn(1)–N(1)	122.40(18)	O(1)–Zn(1)–N(1)	95.67(17)
N(1)[a]–Zn(1)–N(1)	91.7(3)	O(3)[b]–Zn(2)–O(3)	180.0(3)
O(3)–Zn(2)–O(4)	96.51(14)	O(4)[b]–Zn(2)–O(4)	180.0(2)
O(3)–Zn(2)–O(4)[e]	83.49(14)	O(4)–Zn(2)–O(4)[e]	90.9(3)
O(3)–Zn(2)–O(4)[a]	96.51(14)	O(4)–Zn(2)–O(4)[a]	89.1(3)
O(3)[b]–Zn(2)–Zn(4A)	142.42(10)	O(4)–Zn(2)–Zn(4A)	134.05(11)
O(4)[e]–Zn(2)–Zn(4A)	83.29(16)	O(4)[a]–Zn(2)–Zn(4A)	96.71(16)
O(3)–Zn(2)–Zn(4A)[b]	142.42(10)	Zn(4A)–Zn(2)–Zn(4A)[b]	180.0(14)
O(4)–Zn(2)–Zn(4A)	96.71(16)	O(3)–Zn(2)–Zn(4A)[e]	142.42(10)
O(4)–Zn(2)–Zn(4A)[e]	83.29(16)	Zn(4A)–Zn(2)–Zn(4A)[e]	131.32(16)
O(3)[b]–Zn(2)–Zn(4)	138.55(8)	O(4)–Zn(2)–Zn(4)	135.05(10)
O(4)[e]–Zn(2)–Zn(4)	97.18(15)	O(4)[a]–Zn(2)–Zn(4)	82.82(15)
Zn(4A)[b]–Zn(2)–Zn(4)	166.04(3)	Zn(4A)[a]–Zn(2)–Zn(4)	61.22(15)
Zn(4A)[e]–Zn(2)–Zn(4)	118.78(15)	O(3)–Zn(2)–Zn(4)[b]	138.55(8)
Zn(4A)–Zn(2)–Zn(4)[b]	166.04(3)	O(3)–Zn(3)–C(14)	124.1(3)
O(3)–Zn(3)–O(5)	102.42(13)	C(14)–Zn(3)–O(5)	113.03(16)
O(5)–Zn(3)–O(5)[a]	98.3(2)	C(11)–Zn(4)–O(3)	146.2(5)
C(11)–Zn(4)–O(4)[b]	122.4(5)	O(3)–Zn(4)–O(4)[b]	82.71(18)
C(11)–Zn(4)–O(2)	120.7(5)	O(3)–Zn(4)–O(2)	80.1(2)
O(4)[b]–Zn(4)–O(2)	85.5(3)	C(11)–Zn(4)–Zn(2)	145.9(5)
O(2)–Zn(4)–Zn(2)	92.2(2)	O(2)–Zn(4A)–O(3)	107.1(3)
O(2)–Zn(4A)–C(11A)	109.3(5)	O(3)–Zn(4A)–C(11A)	131.1(5)
C(11A)–Zn(4A)–O(2)[a]	126.9(5)	O(3)–Zn(4A)–O(4)[b]	85.56(18)
C(11A)–Zn(4A)–O(4)[b]	113.9(5)	O(2)–Zn(4A)–Zn(4A)[a]	58.3(2)
C(11A)–Zn(4A)–Zn(4A)[a]	148.5(5)	O(3)–Zn(4A)–C(10)	125.1(3)
C(11A)–Zn(4A)–C(10)	99.3(5)	O(4)[b]–Zn(4A)–C(10)	93.3(3)
Zn(4A)[a]–Zn(4A)–C(10)	77.3(2)	O(2)–Zn(4A)–Zn(2)	111.3(3)
C(11A)–Zn(4A)–Zn(2)	138.6(5)	O(2)[a]–Zn(4A)–Zn(2)	94.4(2)
C(10)–Zn(4A)–Zn(2)	115.5(3)	O(2)–Zn(4A)–O(4)[b]	106.0(3)
Compound 7			
Zn(1)–C(12)	1.968(8)	Zn(1)–O(1)	1.975(5)
Zn(1)–N(1)	2.138(7)	Zn(1)–N(4)	2.143(6)
Zn(2)–O(1)	1.986(8)	Zn(2)–C(6)	2.074(7)
C(12)–Zn(1)–O(1)	121.9(4)	C(12)–Zn(1)–N(1)	119.0(3)
O(1)–Zn(1)–N(1)	106.2(2)	C(12)–Zn(1)–N(4)	120.4(4)
O(1)–Zn(1)–N(4)	97.0(2)	N(1)–Zn(1)–N(4)	84.8(2)
O(1)–Zn(2)–C(6)[d]	105.57(19)	O(1)–Zn(2)–C(6)	105.57(19)
C(6)[d]–Zn(2)–C(6)	113.07(16)	O(1)–Zn(2)–C(6)[e]	105.57(19)
C(6)[d]–Zn(2)–C(6)[e]	113.07(16)	C(6)–Zn(2)–C(6)[e]	113.07(16)

[a] x, −y + 1, z. [b] −x + 1, −y + 1, −z. [c] −x + 1, y, −z. [d] −z + 3/2, −x + 1, y + 1/2. [e] −y + 1, z-1/2, −x + 3/2.

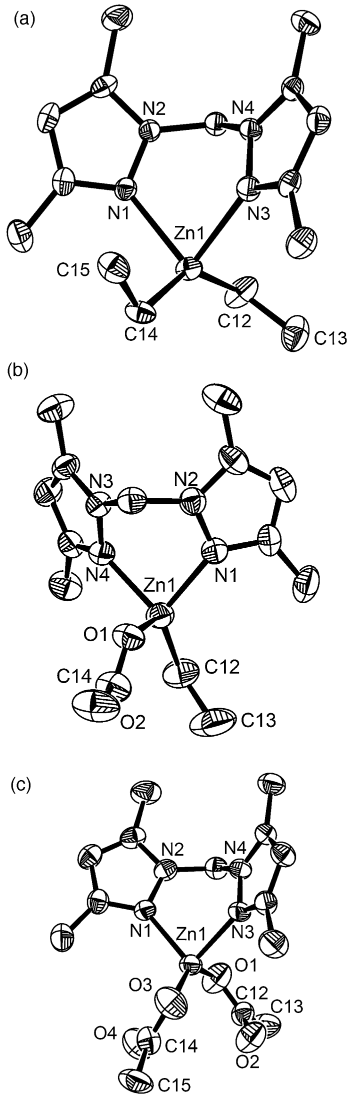


Fig. 1 (a) Molecular structure of **1**. (b) Molecular structure of **3**. (c) Molecular structure of **4**. The thermal ellipsoids are drawn at the 50% probability level and all H atoms are omitted for charity.

monomeric [ZnEt(dmpzm)(HCOO)] molecule. The Zn center is tetrahedrally coordinated by two N atoms from the dmpzm ligand, an ethyl group and a monodentate acetate group (Fig. 1b). The mean Zn–N bond length (2.102(3) Å) is in-between that of the thermolysin[7e] (2.09 Å) and that of **1** while the Zn–O length (1.997(3) Å) is shorter than that in thermolysin (2.08 Å). The Zn–C length is close to those of **1**. The Zn–O distance (1.997(3) Å) is close to those in $[\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}Zn(\mu\text{-}OH)]_3$ (1.909(21) Å).[4c] In the crystal of **3**, an intramolecular hydrogen bonding interaction between the coordinated O atom of the HCOO group and the methylene group, and two intermolecular hydrogen bonding interactions between the uncoordinated O atom of the HCOO group and methyl group, methylene group of the dmpzm ligand producing a dimer of **3**. The distances of these hydrogen bonds are in the range of 2.29–2.54 Å, which are comparable to those found in zinc enzymes.[10] The adjacent [ZnEt(dmpzm)(HCOO)] molecules are also stacked in a face-to-face fashion with a separation of 3.677 Å between the centroids of the two pyrazolyl rings, indicating the existence of the significant intermolecular π–π interactions.

Crystal structure of 4. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit of **4** consists of one monomeric [Zn(dmpzm)(OAc)$_2$] molecule. The Zn atom is coordinated by a dmpzm ligand and a pair of monodentate acetate groups, forming a distorted tetrahedral ZnN_2O_2 geometry (Fig. 1c), which closely resembles those of the zinc active sites in zinc enzymes.[3a,b,7] The average Zn–N and Zn–O bond lengths in **4** (2.096(4) Å *vs* 1.950(5) Å) are slightly shorter than those of the corresponding ones in **3**. In the crystals of **4**, two intramolecular H bonding interactions between the coordinated O atoms of the OAc groups and the methyl group or the methylene group, and three intermolecular H bonding interactions between the uncoordinated O atoms of the OAc groups and the pyrazolyl C–H group of the dmpzm ligand, and the methyl groups and, affording a 3D hydrogen-bonded network. The distances of these hydrogen bonds are in the range of 2.40–2.50 Å, which are comparable to those found in zinc enzymes.[10]

Crystal structure of 6·2C$_7$H$_8$. Compound **6**·2C$_7$H$_8$ crystallizes in the monoclinic space group $C2/m$ and its asymmetric unit contains one-fourth of a [Zn(μ$_4$-O)$_2$(ZnEt)$_6$(μ$_3$-OAc)$_4$(μ′$_3$-OAc)$_2${Zn(dmpzm)Et}$_2$] molecule and one-half of one toluene solvent molecule. This molecule has a mirror plane going through the Zn1, O1, C6, C7, C8, Zn2, O3, Zn3, C13, C14, and their symmetry-related atoms (Fig. 2). It consists of a heptanuclear [Zn(μ$_4$-O)$_2$(ZnEt)$_6$(μ$_3$-OAc)$_4$] core and two [Zn(dmpzm)Et]$^+$ fragments that are held together by a pair of μ′$_3$-OAc ligands. To our knowledge, such a polynuclear Zn structure in **6** is unprecedented, though several other nonanuclear zinc complexes[3a,11] such as [Zn$_6${(RNH)$_3$(RN)$_3$P$_3$N$_3$}$_2$Zn$_3$O$_3$] (R = ^{i}Bu, ^{n}Pr)[3a] and [Zn$_9$(2poap-2H)$_3$(2poap-H)$_3$](NO$_3$)$_9$ (2poap = 2,6-bis(4-amino-4-(pyrid-2-yl)-1-oxy-2,3-diazabuta-1,3-dienyl)pyridine)[11a] were reported. The former example contains a planar (ZnO)$_3$ ring between two cyclic hexamer [Zn$_3${(RNH)$_3$(RN)$_3$P$_3$N$_3$}] fragments, while the latter has a [Zn$_9$(μ-O)$_{12}$] plane.

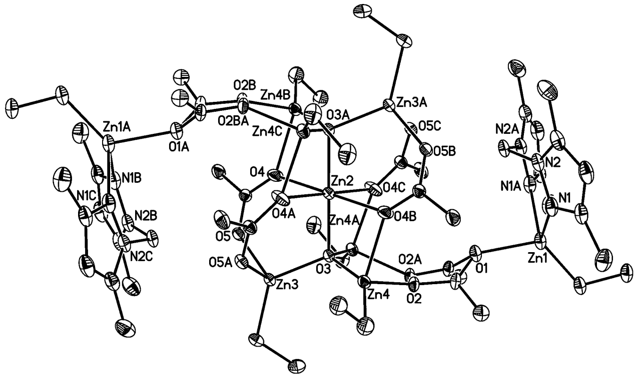


Fig. 2 Perspective view of **6** showing 30% thermal probability ellipsoids. The disordered moieties, solvent molecules and hydrogen atoms are omitted for charity.

The [Zn(μ$_4$-O)$_2$(ZnEt)$_6$(μ$_3$-OAc)$_4$] core in **6** has a [Zn$_7$(μ$_4$-O)$_2$] double tetrahedron core in which two tetrahedral Zn(μ$_4$-O)(ZnEt)$_3$ units share a vertex *via* the Zn2 atom and are linked by four μ$_3$-OAc bridges (Fig. 3). The central Zn2 is coordinated by two μ$_4$-O atoms (occupying the axial positions) and four O atoms from four acetate groups (locating on the equatorial plane), thus forming a distorted octahedral coordination geometry. Such a [Zn$_7$(μ$_4$-O)$_2$] double tetrahedron core in **6** resembles those found in the known discrete complexes[12] and polymeric structures.[13] The difference between the [Zn$_7$O$_2$(RCO$_2$)$_{10}$] motif in those reported complexes and the [Zn(μ$_4$-O)$_2$(ZnEt)$_6$(μ$_3$-OAc)$_4$] core in **6** is that the former has ten caboxylate groups around its Zn$_7$(μ$_4$-O)$_2$ core while the peripheral ligation around the latter core is provided by four acetate groups along with six ethyl groups.

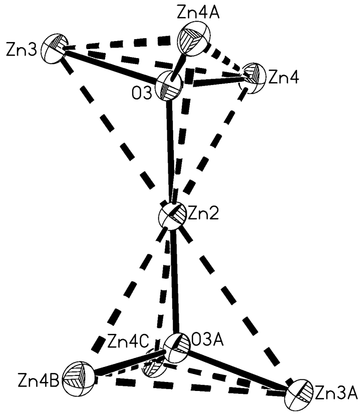


Fig. 3 View of the [Zn$_7$(μ$_4$-O)$_2$] skeleton of **6** showing the vertex shared double tetrahedron.

For each Zn(μ$_4$-O)(ZnEt)$_3$ unit, a μ$_4$-O3 or μ$_4$-O3A atom connects Zn2 and three ZnEt fragments. Each Zn in these ZnEt fragments exhibit a distorted tetrahedral environment and is saturated by an ethyl group and two O atoms from acetate groups. For each [Zn(dmpzm)Et]$^+$ fragment, Zn1 or Zn1A is tetrahedrally coordinated by a C atom from ethyl groups and a O atom from acetate group and two N atoms from dmpzm groups. It is noted that there are two kinds of triply-bridging OAc ligands. One links Zn2, Zn3A, Zn4 (or Zn4A) or Zn2, Zn3, Zn4B (or Zn4C) while the other disordered over two positions and bridges Zn1, Zn4 (or Zn4A) or Zn1A, Zn4B (or Zn4C). The mean Zn–N, Zn–O znd Zn–C bond lengths are normal.

Crystal structure of 7. Compound **7** crystallizes in the cubic space group $P2_13$ and its asymmetric unit has one-third of a [Zn$_4$(μ$_4$-O)(dmpzm)$_3$Et$_3$] molecule. The whole molecule possesses a C_3 axis running along the Zn2–O1 bond (Fig. 4). The μ$_4$-O atom lies at the center of the Zn4 tetrahedron and interacts with four Zn atoms, with Zn–μ$_4$-O lengths ranging from 1.974(2) to 1.986(8) Å. The Zn$_4$(μ$_4$-O) tetrahedron is slightly irregular with the Zn ··· Zn distances being between 3.167 and 3.284 Å. Each Zn atom in this tetrahedron displays a distorted tetrahedral geometry. Zn1, Zn1A or Zn1B is saturated by two N atoms from dmpzm ligands and an ethyl group, while Zn2 binds to three C atoms from the methylene group of the three dmpzm ligands. This is quite unusual that one methylene proton of the dmpzm ligand was removed during the reactions. The Zn2–C6 bond distance (2.074(7) Å) is longer than that of Zn1–C12 bond (1.968(8) Å), but within the range for Zn–C-alkyl distances.[9] The mean Zn–N bond length (2.140(6) Å) is somewhat shorter than that in **1**. The adjacent [Zn$_4$(μ$_4$-O)(dmpzm)$_3$Et$_3$] molecules are stacked in a face-to-face fashion with a separation of 3.684 Å between the centroids

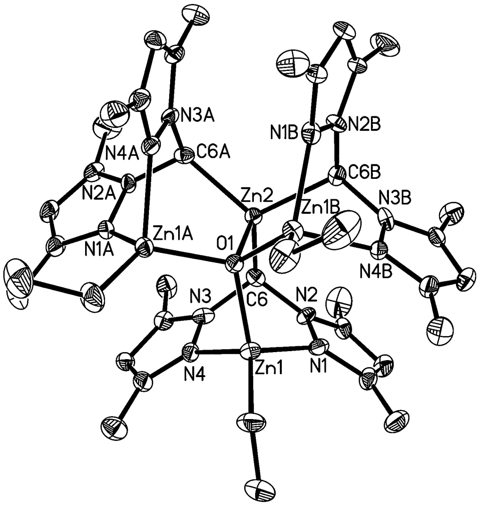


Fig. 4 Perspective view of **7** showing 30% thermal probability ellipsoids. All hydrogen atoms are omitted for charity.

of the two pyrazolyl rings, showing the existence of the significant intermolecular π–π interactions.

For **6** and **7**, two important phenomena deserve comment. One is that both contain one or two μ_4-O atoms in their structures. These μ_4-O atoms may be derived from the small amount of water in organic acids used in the reactions. In fact, the direct addition of 1/4–1/10 equiv. of water into the mixture of **1** and acetic acid always produced **6** in low yields, while **7** could be readily obtained in relative high yields from reactions of **1** with 1/4–1/8 equiv. of H_2O in toluene. The other is that during the protonolysis reaction some Zn centers still retained one Et group while some lost the dmpzm ligand. In **6**, the central Zn2 atom lost two Et groups and the dmpzm ligands while Zn3 and Zn4 and their symmetry-related atoms only kept one Et group, and Zn1 or Zn1A retained one Et group and one dmpzm ligand. In **7**, the central Zn2 lost all Et groups and the dmpzm ligand while the rest Zn atoms only lost one Et group. The loss of the dmpzm ligand from the Zn center of **6** and **7** may be a proof of the reversibly of zinc to the soft donor.[3a]

Conclusions

In this paper, we have demonstrated that the protonolysis reaction of **1** with acetic or formic acid was stoichiometric-dependent. Only the 1 : 2 mixture of **1** and the acid could afford the desired $[ZnN_2O_2]$ complexes (**4** and **5**) while those with other molar ratios could produce mononuclear complexes (**2** and **3**) and polynculear complexes (**6** and **7**). These results may provide interesting insight into the reactivity of similar alkylzinc complexes toward acids and a useful route to other zinc model complexes mimicking the active sites in some zinc-containing enzymes.

Acknowledgements

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