Supporting Information

Oxygenation of Alkylzinc Complexes with Pyrrolylketiminate Ligand: Access to Alkylperoxide versus Oxo-Encapsulated Complexes

Janusz Lewiński,[a,b] Karolina Suwała,[a] Tomasz Kaczorowski,[a] Michał Gałęzowski,[c] Daniel T. Gryko,[c] Iwona Justyniak*[b] and Janusz Lipkowski[b]*

[a] *Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland. Fax: +48 22 234 7279; Tel: +48 22 234 7315; E-mail: lewin@ch.pw.edu.pl*

[b] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

[c] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.*

Experimental Section

General experimental procedures: All operations were carried out under dry nitrogen using standard Schlenk techniques. $^{t}Bu_2Zn$[1] and 2,2'-(1'-pyrroliny1)-pyrrole (*Pyr-pyrl*)[2] were synthesized according to the literature method. Hexane and toluene were distilled from sodium-benzophenone. NMR spectra were recorded on a Varian Mercury 400 Spectrometer.

Synthesis of [EtZn(*Pyr-pyrl*)] (1). A solution of 2,2'-(1'-pyrrolinyl)-pyrrole (0.155 g, 1.15 mmol) in toluene (4 mL) was cooled to -78°C, and Et_2Zn (0.46 mL of a 2.49 M solution in toluene, 1.15 mmol) was added dropwise. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 2 h. ^1H NMR (400 MHz, C_6D_6): δ, ppm, 0.23 (2H, q, -ZnCH_2CH$_3$), 1.24 (3H, t, -ZnCH$_2$CH_3), 1.44 (2H, t, C$H_{2\mathrm{pyrl}}$), 2.29 (2H, t, C$H_{2\mathrm{pyrl}}$), 3.20 (2H, t, C$H_{2\mathrm{pyrl}}$), 6.52 (1H, s, CH_{pyr}), 6.68 (1H, s, CH_{pyr}), 6.97 (1H, s, CH_{pyr}).

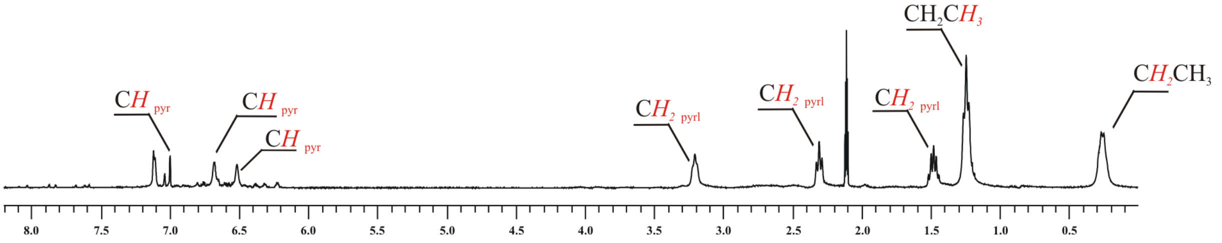

Figure S1. ^1H NMR spectrum of **1** (400 MHz, C_6D_6).

Synthesis of [^{t}BuZn(*Pyr-pyrl*)] (2). A solution of 2,2'-(1'-pyrroliny1)-pyrrole (0.179 g, 1.33 mmol) in toluene (5 mL) was cooled to -78°C, and $^tBu_2Zn$ (1.0 mL of a 1.4 M solution in toluene, 1.33 mmol) was added dropwise. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 2 h; then the volatiles were removed in vacuo. Complex **2** was obtained as colorless crystals after a recrystallization from toluene solution at -25°C (0.34 g, 92%). Elemental analysis (%) calcd for $C_{12}H_{18}N_2Zn$: C 56.37, H 7.09, N 10.96; found: C 56.31, H 7.06, N 10.99. ^1H NMR (400 MHz, C_6D_6): δ, ppm, 1.26 (9H, s, -ZnC(CH_3)$_3$), 1.38 (2H, m, C$H_{2\mathrm{pyrl}}$), 2.31 (2H, t, C$H_{2\mathrm{pyrl}}$), 3.24 (2H, t, C$H_{2\mathrm{pyrl}}$), 6.67 (1H, s, CH_{pyr}), 6.84 (1H, s, CH_{pyr}), 7.25 (1H, s, CH_{pyr}).

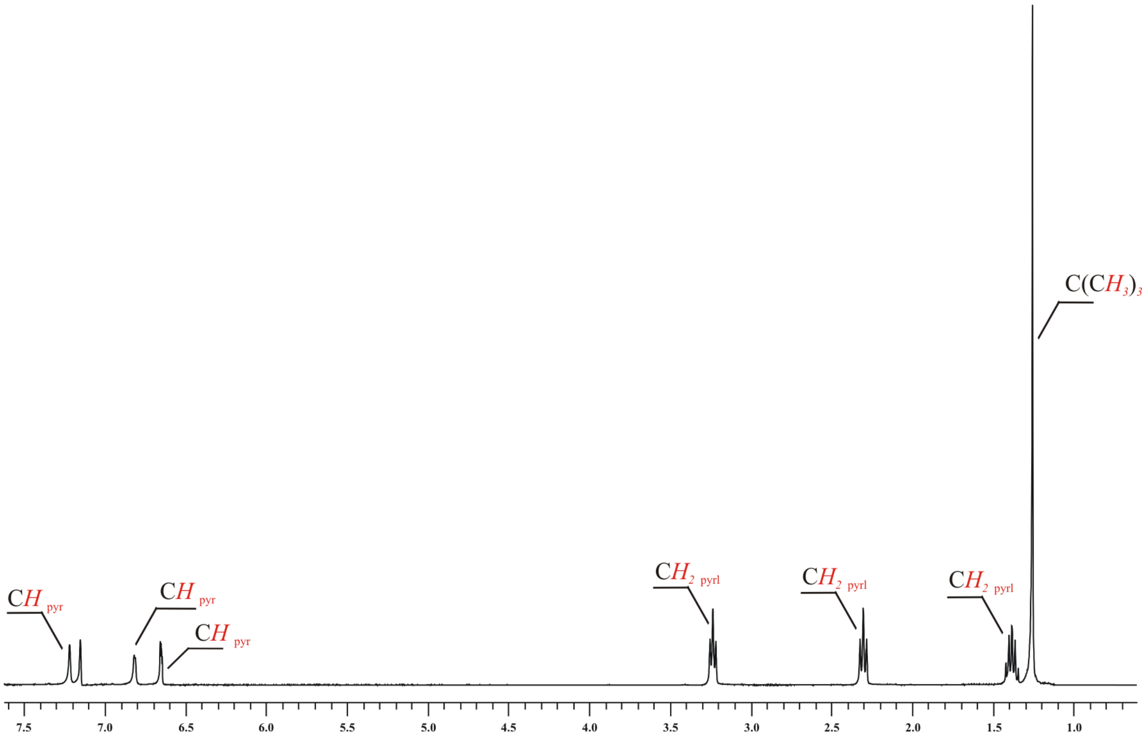

Figure S2. ^{1}H NMR spectrum of **2** (400 MHz, C_6D_6).

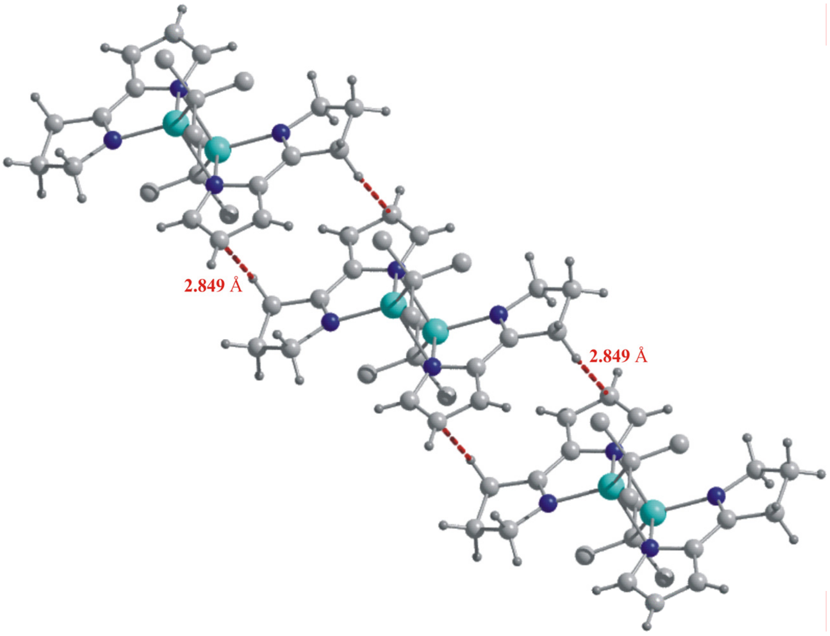

Figure S3. The crystal structure of **2** showing weak non-covalent C–H…π interactions between monomeric units.

Synthesis of [^{t}BuOOZn(*Pyr-pyrl*)]$_2$[Zn(*Pyr-pyrl*)$_2$] (3). A solution of **2** (0.34 g, 1.33 mmol) in toluene (5mL) was cooled to -20ºC and exposed to an excess of dry oxygen for the 20 min.. After oxygenation the excess O_2 was removed, and the system was purged with nitrogen by using a vacuum-nitrogen line. The resulting compound [^{t}BuOOZn(*Pyr-pyrl*)]$_2$[Zn(*Pyr-pyrl*)$_2$] was deposited from a toluene solution at -15ºC after 4 hours as a colorless square-shaped crystals (0.024 g, 80%). Elemental analysis (%) calcd for $C_{40}H_{54}N_8Zn_3O_4$: C 52.96, H 6.00, N 12.35; found: C 52.92, H 5.94, N 12.39. ^{1}H NMR (400 MHz, C_6D_6): δ, ppm, 1.13 (d, 9H, $(CH_3)_3$C-Zn), 1.36 (s, 9H, $(CH_3)_3$C-

Zn), 1.54 (8H, m, C$H_{2\mathrm{pyrl}}$), 2.33 (8H, m, C$H_{2\mathrm{pyrl}}$), 3.26 (8H, m, C$H_{2\mathrm{pyrl}}$), 6.69 (4H, s, CH_{pyr}), 6. 90 (4H, s, CH_{pyr}), 7.30 (4H, s, CH_{pyr}).

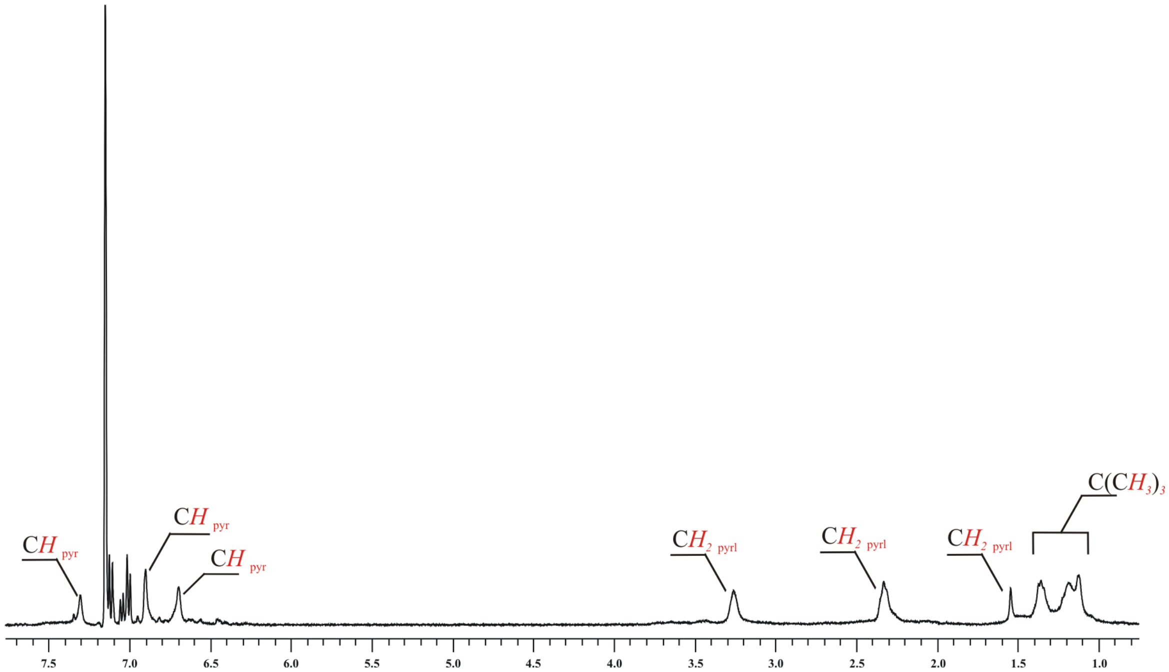

Figure S4. ^{1}H NMR spectrum of **3** (400 MHz, C_6D_6).

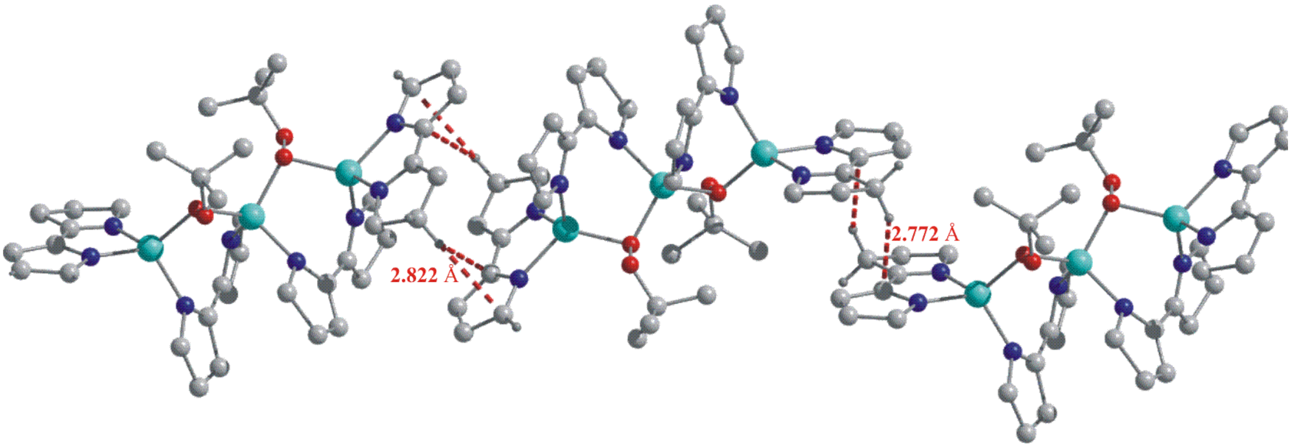

Figure S5. The crystal structure of **3** showing weak non-covalent C–H…π interactions between monomeric units.

Synthesis of [$Zn_4(\mu_4\text{-}O)$(*Pyr-pyrl*)$_6$] (4). A reaction mixture of **1**,which was prepared in reaction of 2,2'-(1'-pyrroliny1)-pyrrole (0.156 g, 1.16 mmol) with Et_2Zn (0.45 mL of a 2.56 M solution in toluene, 1.16 mmol) in toluene (4 mL) in toluene (5mL) was cooled to -20ºC and exposed to an excess of dry oxygen for the 30 min.. After oxygenation the excess O_2 was removed, and the system was purged with nitrogen by using a vacuum-nitrogen line. The resulting compound [$Zn_4(\mu_4\text{-}O)$(*Pyr-pyrl*)$_6$] was deposited from a toluene solution at -15ºC after 3 days as a colorless crystals (0.135 g, 65%). Elemental analysis (%) calcd for $C_{48}H_{54}N_{12}Zn_4O$: C 53.55, H 5.05, N 15.61; found: C 53.52, H 5.08, N 15.57. ^{1}H NMR (400 MHz, C_6D_6): δ, ppm, 1.38 (2H, m, C$H_{2\mathrm{pyrl}}$), 2.35 (2H, m, C$H_{2\mathrm{pyrl}}$), 3.42 (2H, m, C$H_{2\mathrm{pyrl}}$), 6.58 (1H, s, CH_{pyr}), 6.68 (1H, s, CH_{pyr}), 7.10 (1H, s, CH_{pyr}).

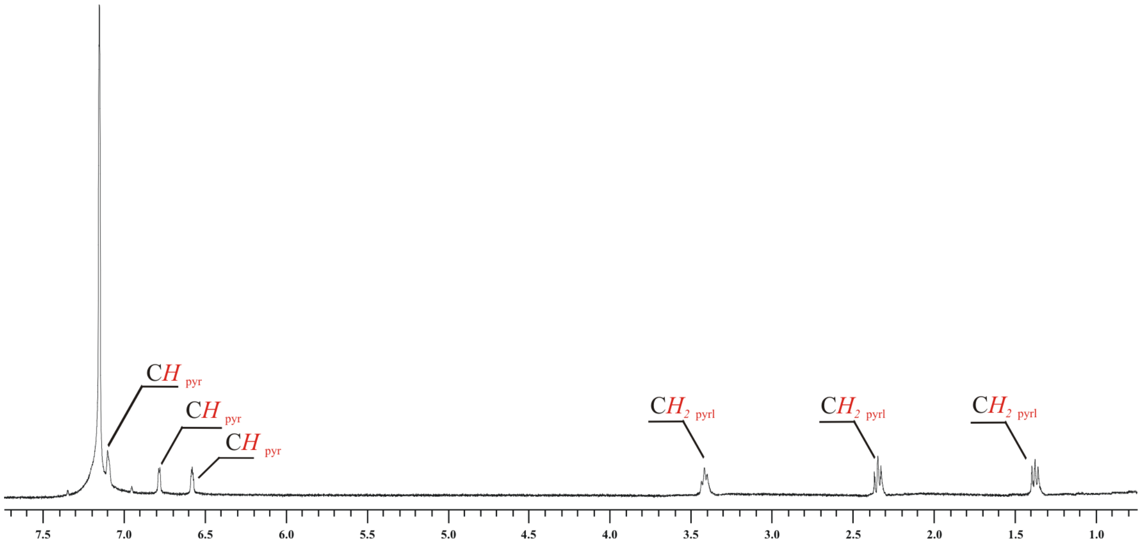

Figure S6. ^{1}H NMR spectrum of **4** (400 MHz, C_6D_6).

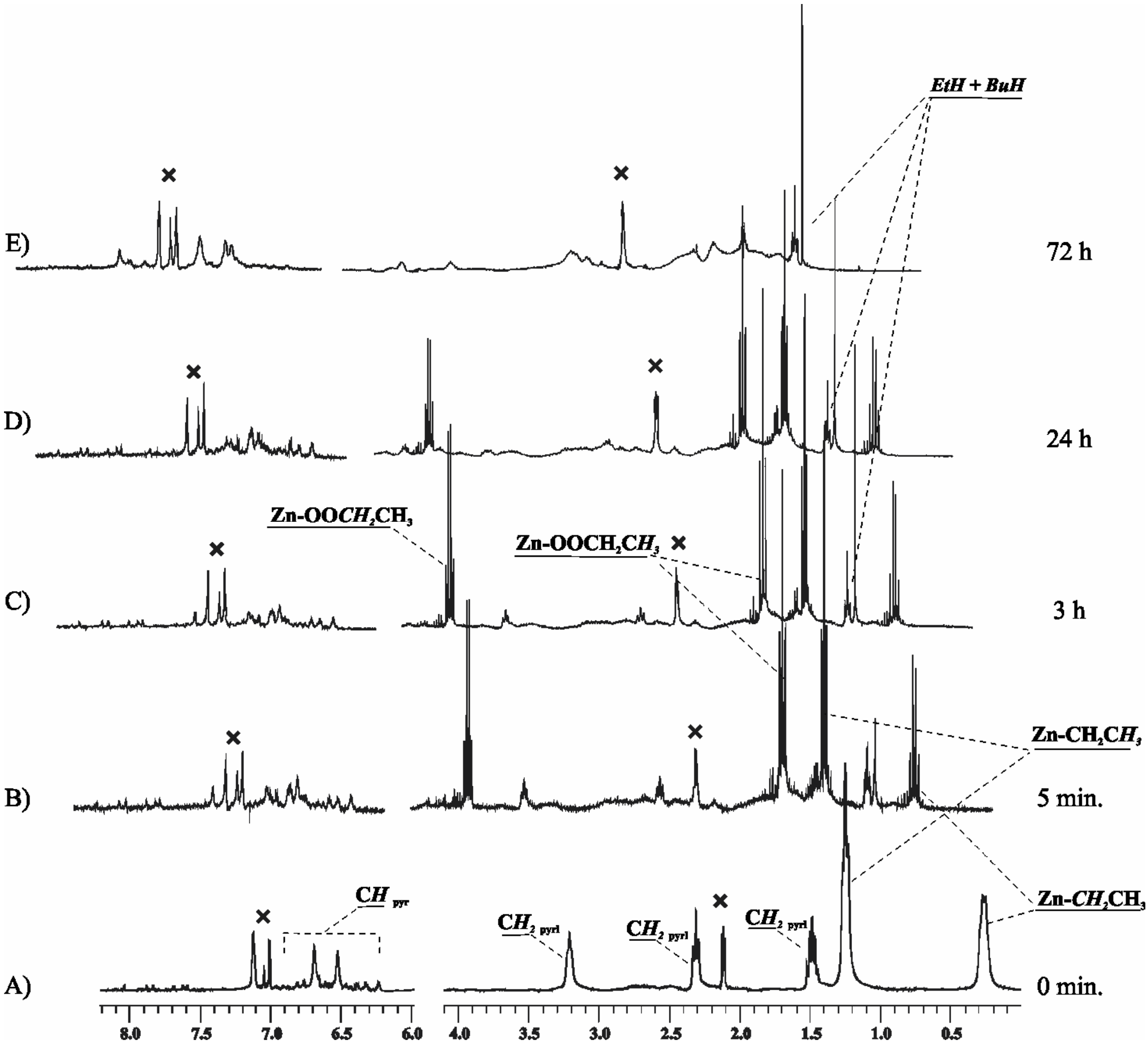

Figure S7. Representative ^{1}H NMR spectra for the oxygenation of **1** in toluene-d^8 at -20ºC: before introduction of O_2 (A); during the reaction with O_2: 5 min. (B), 3 h (C), 24 h (D) and 72 h (E); peaks marked with **x** represent signals of the solvent.

X-Ray structure determination

Crystal data for **[^{t}BuZn(*Pyr-pyrl*)]** (**2**), $C_{24}H_{36}N_4Zn_2$: *M* = 511.31, crystal dimensions 0.64 × 0.42 × 0.34 mm^3, triclinic, space group *P*-1 (no. 2), *a* = 8.3637(2) Å, *b* = 8.7342(3) Å, *c* = 9.4312(3) Å, α = 105.1357(11)°, β = 104.473(2)°, γ = 104.829(2)°, *U* = 604.73(3) Å^3, *Z* = 1, *F*(000) = 268, D_c = 1.404 g m^3, *T* = 100(2)K, μ(Mo-Kα) = 2.00 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 27.56°, 2775 unique reflections. The structure was solved by direct methods using the SHELXS97[3] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2 or 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon. Refinement converged at *R*1 = 0.0276, *wR*2 = 0.0563 for all data and 172 parameters (*R*1 = 0.0254, *wR*2 = 0.0554 for 2631 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.044. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.41 /-0.31 eÅ^{-3}. ORTEP drawings were made using ORTEP3 for Windows.[5]

Crystal data for **[^{t}BuOOZn(*Pyr-pyrl*)]$_2$[Zn(*Pyr-pyrl*)$_2$]** (**3**), $C_{40}H_{54}N_8Zn_3O_4$·*toluene*: *M* = 999.22, crystal dimensions 0.49 × 0.26 × 0.22 mm^3, triclinic, space group *P*-1 (no. 2), *a* = 14.6481(3) Å, *b* = 18.5359(3) Å, *c* = 18.7841(4), α = 92.2702(10)°, β = 98.1488(10)°, γ = 94.0181(10)°, *U* = 5029.93(17) Å^3, *Z* = 4, *F*(000) = 2088, D_c = 1.319 g m^3, *T* = 100(2)K, μ(Mo-Kα) = 1.47 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 22.72°, 13525 unique reflections. The structure was solved by direct methods using the SHELXS97[3] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2 or 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon. Refinement converged at *R*1 = 0.0808, *wR*2 = 0.1701 for all data, 1130 parameters, and 29 restraints (*R*1 = 0.0647, *wR*2 = 0.1584 for 10061 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.106. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.73/-0.51 eÅ^{-3}. ORTEP drawings were made using ORTEP3 for Windows.[5]

Disorder associated with the *tert*-butyl groups and peroxide groups was noted. Of particular significance were the observations of two positions each for the methyl carbons [C(2) – C(4)] and [C(46) – C(48)] of the *tert*-butyl groups (in a 3 : 1 and 7 : 3 ratio respectively). The groups showing SOF = 25 and SOF = 30 were refined isotropically with geometrical restrains assuming that chemical distances in both groups were nearly equal. In the case of peroxide groups' disorder, for one group the disorder was modeled in terms of two sets of –[O(1)O(2)] atoms with refined occupancy factors 0.75 and 0.25. The group showing SOF = 0.25 was refined isotropically. For the second peroxide group the best model that could be developed was the one in which we observed two positions of the oxygen atom [O(8)] of a peroxide group (in a molar ratio 7 : 3). The toluene molecule, which acted as a solvent, was also disordered. The disorder was modeled in terms of two sets of carbons atoms with refined occupancy factors 0.67(1) and 0.33(1). The group showing SOF = 0.33(1) was refined isotropically.

Crystal data for **[Zn$_4$(μ$_4$-O)(*Pyr-pyrl*)$_6$]** (**4**), $C_{48}H_{54}N_{12}Zn_4O$: M = 1076.17, crystal dimensions 0.42 × 0.24 × 0.18 mm^3, monoclinic, space group *C* 2/c (no. 15), a = 22.1870(13) Å, b = 17.1310(12) Å, c = 19.3830(12) Å, β = 122.651(3)°, U = 6203.0(7) Å^3, Z = 4, F(000) = 2144, Dc = 1.153 g m^3, T = 100(2)K, μ(Mo-Kα) = 1.57 mm^{-1}, Nonius Kappa-CCD diffractometer, $\theta_{\max}$ = 21.97°, 3721 unique reflections. The structure was solved by direct methods using the SHELXS97[3] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[4] H-atoms were included in idealized positions and refined isotropically. Refinement converged at R1 = 0.0663, wR2 = 0.1395 for all data and 294 parameters (R1 = 0.0543, wR2 = 0.1325 for 3093 reflections with $Io > 2\sigma(Io)$). The goodness-of-fit on F^2 was equal 1.076. A weighting scheme w = [σ2(Fo2 + (0.0418P)2 + 3.1964P]-1, where P = (Fo2 + 2Fc2)/3, was used in the final stage of refinement. The residual electron density = +0.40/-0.35 eÅ^{-3}. ORTEP drawings were made using ORTEP3 for Windows.[5]

The determination of compounds **3** and **4** was conducted using narrower theta angles, because at wider angles the diffraction was not observed. Secondly, based on our experiences concerning the stability of metal alkylperoxides, the shortest as far as possible measuring time is always recommended. The structures of compounds **3** and **4** shown relatively large solvent-accessible voids, however the observed low residual electron densities indicate that those voids remained empty.

---

[1] H. Lehmkuhl, O. Liebigs, *Ann. Chem.,* 1975, 1162.

[2] Rapoport, H.; Castagnoli, N. *J. Am. Chem. Soc*., 1962, **84**, 2178.

[3] "SHELXS-97, *Program for Structure Solution*": G.M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467.

[4] Sheldrick, G. M. SHELXL-97, Program for Structure Refinement, Universität Göttingen, 1997.

[5] Farrugia, L. J. *J. Appl. Cryst.,* 1997, **30**, 565.