Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting Information: anie.200800870

Self-Assembly of a Cyclic Zn_4O_4 Tetramer by Aerobic Oxidation of a Bisoxazoline: A Molecular "Nest" for Nucleophilic OH^-

Béatrice Jacques, Clémence Dro, Stéphane Bellemin-Laponnaz,*
Hubert Wadepohl and Lutz H. Gade*

Contents:

1) Preparation of Compounds 2-4

MeOH was either distilled over $MgSO_4$ or purchased from Aldrich (HPLC Grade) and used as received. The bisoxazoline Me_2BOX was prepared according to published procedures.[1] All other reagents were obtained from commercial sources and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance II 400 and 600 NMR spectrometers and were referenced using residual proton or ^{13}C solvent peaks. IR spectra were recorded on a Varian 3100 FT-IR spectrometer. Mass spectra and elemental analyses were recorded by the analytical services of Heidelberg University or Strasbourg University. ***Caution:*** *perchlorates are known to be potentially explosive. These compounds should be handled with care only on a millimolar scale using appropriate safety precautions.*

Preparation of complex $[\{Me_2BOX\text{-}O\}_4Zn_4(OH)][ClO_4]_3$ **2**: 1,1-Bis[4,4-dimethyloxazolin-2-yl]ethane **1** (0.152 g, 0.68 mmol) was dissolved in methanol (5 mL). $Zn(ClO_4)_2.6H_2O$ (0.229 g, 0.62 mmol) and $NaHCO_3$ (0.067 g, 0.80 mmol) were then added and the mixture was stirred in air for 24 hours. The white precipitate obtained was isolated by filtration, washed with diethylether and then dissolved in dichloromethane. The solution was filtered on Celite. Addition of hexanes and evaporation under reduce pressure gave compound **2** as a white powder (0.207 g, 0.135 mmol, 88%). Recrystallization from CH_2Cl_2/hexane gave colorless crystals suitable for X-ray diffraction. ^1H NMR (400 MHz, $(CD_3)_2CO$): δ = 1.41 (s, 24H; $C(CH_3)_2$), 1.61 (s, 24H; $C(CH_3)_2$), 1.81 (s, 12H; CH_3), 4.44 (d, ^2J(H,H) = 8.0 Hz, 8H; CH_2), 4.63 (d, ^2J(H,H) = 8.0 Hz, 8H; CH_2) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$): δ = 28.3 ($C(CH_3)_2$), 29.7 (C(oxazoline)$_2$(O)(CH_3)), 30.6 ($C(CH_3)_2$), 67.9 ($C(CH_3)_2$), 72.3 (C(oxazoline)$_2$(O)(CH_3)), 86.1 (CH_2), 177.8 (C=N) ppm; FT-IR (KBr): $\tilde{\nu}$ = 1095 (C–O), 1151 (C–O), 1647 (C=N), 1661 (C=N) cm^{-1}; HRMS (ESI): *m/z* (%): 1427.1732 (100%) ($\{[\{Me_2BOX\text{-}O\}_4Zn_4(OH)][ClO_4]_2\}^+$, calculated for $C_{48}H_{77}Cl_2N_8O_{21}Zn_4$: 1427.1741); elemental analysis (%) calcd for $C_{48}H_{77}Cl_3N_8O_{25}Zn_4$: C 37.58, H 5.06, N 7.30; found C 37.59, H 5.21, N 7.14.

Preparation of complex $[\{Me_2BOX\text{-}^{18}O\}_4Zn_4(OH)][ClO_4]_3$ **2a**: Under a nitrogen atmosphere, a solution of 1,1-bis[4,4-dimethyloxazolin-2-yl]ethane **1** (0.152 g, 0.68 mmol) in distilled methanol (5 mL) was added to $Zn(ClO_4)_2.6H_2O$ (0.229 g, 0.62 mmol) and $NaHCO_3$ (0.067 g, 0.80 mmol). The solution was degassed by three freeze-pump-thaw cycles. At room temperature, the flask was then filled with $^{18}O_2$ gas (isotopic purity 99%, purchased from Aldrich) and the reaction mixture was stirred for 24 hours. The white precipitate obtained was isolated by filtration, washed with diethylether and then dissolved in dichloromethane. The solution was filtered on Celite. Addition of hexanes and evaporation under reduce pressure gave compound **2a** as a white powder (0.083 g, 0.054 mmol, 35%). The ^1H NMR spectrum is

[1] S. Dagorne, S. Bellemin-Laponnaz, R. Welter, *Organometallics* **2004**, *23*, 3053-3061.

the same as for complex **2**. FT-IR (KBr): $\tilde{\nu}$ = 1095 (C–O), 1144 (C–O), 1647 (C=N), 1661 (C=N) cm^{-1}; HRMS (ESI): *m/z* (%): 1435.1918 (100%) ({[{Me_2BOX-^{18}O}$_4$$Zn_4$(OH)][$ClO_4$]$_2$}$^+$, calculated for $C_{48}H_{77}Cl_2N_8O_{17}{}^{18}O_4Zn_4$: 1435.1911); elemental analysis (%) calcd for $C_{48}H_{77}Cl_3N_8O_{21}{}^{18}O_4Zn_4$: C 37.39, H 5.03, N 7.27; found C 37.67, H 5.01, N 7.00.

Preparation of complex [(Me_2BOX)Zn(H_2O)$_3$](ClO_4)$_2$ **3**. Under an argon atmosphere, a solution of 1,1-bis[4,4-dimethyloxazolin-2-yl]ethane **1** (0.148 g, 0.66 mmol) in distilled methanol (3 mL) was added to a solution of Zn(ClO_4)$_2$.6H_2O (0.223 g, 0.60 mmol) in distilled methanol (2 mL). The reaction mixture was stirred under argon at room temperature for 24 hours. The white precipitate obtained was isolated by filtration and washed with diethylether giving **3** as a white powder (0.087 g, 0.16 mmol, 27%). ^{1}H NMR (600 MHz, (CD_3)$_2$CO): δ = 1.62 (s, 12H; C(CH_3)$_2$), 1.65 (d, ^3J(H,H) = 7.8 Hz, 3H; C*H*CH_3), 4.07 (q, ^3J(H,H) = 7.8 Hz, 1H; CHC*H*$_3$), 4.40 (s, 4H; CH_2) ppm; ^{13}C{^{1}H} NMR (150 MHz, (CD_3)$_2$CO): δ = 17.0 (CH*C*H_3), 29.7 (C(*C*H_3)$_2$), 35.1 (*C*HCH$_3$), 69.7 (*C*(CH_3)$_2$), 82.1 (CH_2), 172.9 (C=N) ppm; FT-IR (KBr): $\tilde{\nu}$ = 1663 (C=N) cm^{-1}; HRMS (ESI): *m/z* (%): 305.0841 (20%) ([(Me_2BOX)Zn(OH)]$^+$, calculated for $C_{12}H_{21}N_2O_3Zn$: 305.0838).

Preparation of complex [(Me_2BOX)Zn(H_2O)$_3$](OTf)$_2$ **3a.** Under an argon atmosphere, a solution of 1,1-bis[4,4-dimethyloxazolin-2-yl]ethane **1** (0.100 g, 0.45 mmol) in methanol (1.5 mL) was added to a solution of Zn(OTf)$_2$ (0.147 g, 0.41 mmol) in methanol (0.5 mL). The reaction mixture was stirred under argon at room temperature for 2 hours. MeOH was removed in vacuo and the resulting solid washed twice with hexane giving **3a** as a white solid (0.208 g, 0.32 mmol, 78%). Recrystallization from CH_2Cl_2/hexane gave colorless crystals suitable for X-ray diffraction. ^{1}H NMR (400 MHz, (CD_3)$_2$CO): δ = 1.54 (s, 6H; C(CH_3)$_2$), 1.55 (s, 6H; C(CH_3)$_2$), 1.72 (d, ^3J(H,H) = 7.6 Hz, 3H; C*H*CH_3), 4.19 (q, ^3J(H,H) = 7.6 Hz, 1H; CHC*H*$_3$), 4.51 (s, 4H; CH_2) ppm; ^{13}C{^{1}H} NMR (100 MHz, (CD_3)$_2$CO): δ = 17.8 (CH*C*H_3), 28.2 (C(*C*H_3)$_2$), 28.3 (C(*C*H_3)$_2$), 36.0 (*C*HCH$_3$), 69.9 (*C*(CH_3)$_2$), 82.6 (CH_2), 174.1 (C=N) ppm; IR (KBr): $\tilde{\nu}$ = 1670 (C=N) cm^{-1}; MS (FAB): *m/z* (%): 623.1 (49%) (M-OH$^-$); HRMS (ESI): *m/z* (%): 305.0842 (26%) ([(Me_2BOX)Zn(OH)]$^+$, calculated for $C_{12}H_{21}N_2O_3Zn$: 305.0838), 437.0337 (72%) ({[(Me_2BOX)Zn][CF_3SO_3]}$^+$, calculated for $C_{13}H_{20}F_3N_2O_5SZn$: 437.0331); elemental analysis (%) calcd for $C_{14}H_{26}F_6N_2O_{11}S_2Zn$: C 26.20, H 4.08, N 4.36; found C 26.09, H 4.02, N 4.21.

Preparation of complex [{Me_2BOX-O}$_4$$Zn_4$][$ClO_4$]$_3$[$BF_4$] **4**. Under a nitrogen atmosphere, a solution of **2** (58 mg, 0.031 mmol) in distilled CH_2Cl_2 (3 mL) was cooled to 0°C. HBF_4 (50 µL, 0.031 mmol, 10 times diluted tetrafluoroboric acid, 50-54% w/v in diethylether) was then added. The reaction was stirred at 0°C for 15 minutes and then at room temperature for an hour. Evaporation of the solvents under reduced pressure then gave **4** (50 mg, 0.031 mmol) as a white solid in quantitative yield. Recrystallisation from acetone/hexane gave colorless crystals suitable for X-ray diffraction analysis. ^{1}H NMR (400 MHz, (CD_3)$_2$CO): δ = 1.51 (s, 24H; C(CH_3)$_2$), 1.54 (s, 24H; C(CH_3)$_2$), 1.90 (s, 12H; CH_3), 4.56 (d, ^2J(H,H) = 8.8 Hz, 8H; CH_2), 4.73 (d, ^2J(H,H) = 8.8 Hz, 8H; CH_2) ppm; ^{13}C{^{1}H} NMR (100 MHz, (CD_3)$_2$CO): δ = 29.1 (C(*C*H_3)$_2$), 29.7 (C(*C*H_3)$_2$), 30.0 (C(oxazoline)$_2$(O)(*C*H_3)), 67.8 (*C*(CH_3)$_2$), 72.7 (*C*(oxazoline)$_2$(O)(CH_3)), 86.7 (CH_2), 178.1 (C=N) ppm; FT-IR (KBr): $\tilde{\nu}$ = 1099 (C–O), 1147 (C–O), 1655 (C=N) cm^{-1}; HRMS (ESI): *m/z* (%): 664.1140 (4%) ({[{Me_2BOX-O}$_4$$Zn_4$(OH)][$ClO_4$]}$^{2+}$, calculated for $C_{48}H_{77}ClN_8O_{17}Zn_4$: 664.1131), 705.0874 (6%) ({[{Me_2BOX-O}$_4$$Zn_4$][$ClO_4$]$_2$}$^{2+}$, calculated for $C_{48}H_{76}Cl_2N_8O_{20}Zn_4$: 705.0854), 1427.1786 (100%) ({[{Me_2BOX-O}$_4$$Zn_4$(OH)][$ClO_4$]$_2$}$^+$, calculated for $C_{48}H_{77}Cl_2N_8O_{21}Zn_4$: 1427.1741); elemental analysis (%) calcd for $C_{48}H_{76}BCl_3F_4N_8O_{24}Zn_4$: C 35.94, H 4.78, N 6.99; found C 36.40, H 5.28, N 6.43.

2) IR Study of Complexes 2 and 2a

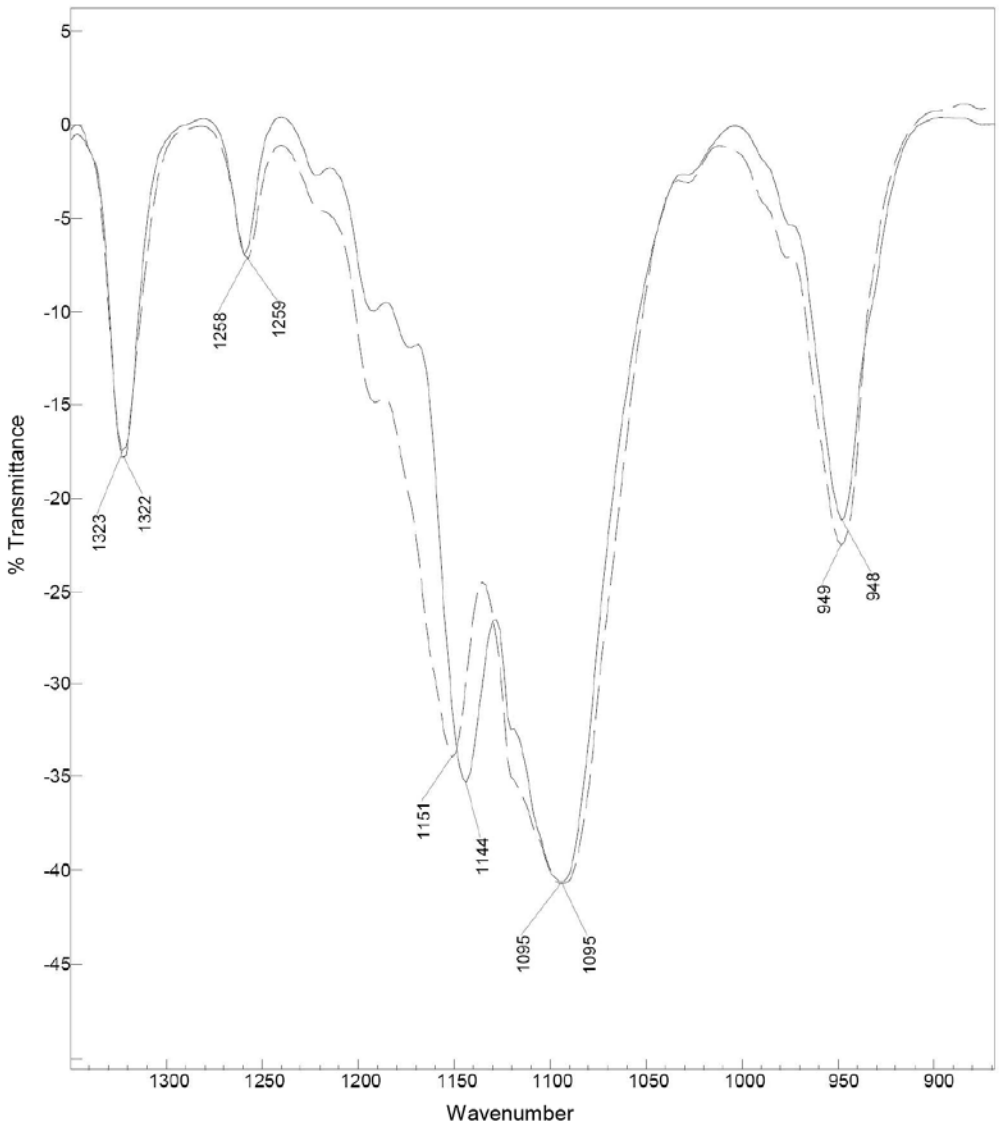

Figure S1. IR spectra (KBr) of complex [{Me_2BOX-O}$_4$$Zn_4$(OH)][$ClO_4$]$_3$ **2** (dashed line) and complex [{Me_2BOX-^{18}O}$_4$$Zn_4$(OH)][$ClO_4$]$_3$ **2a** (solid line).

3) Molecular structure of 3a

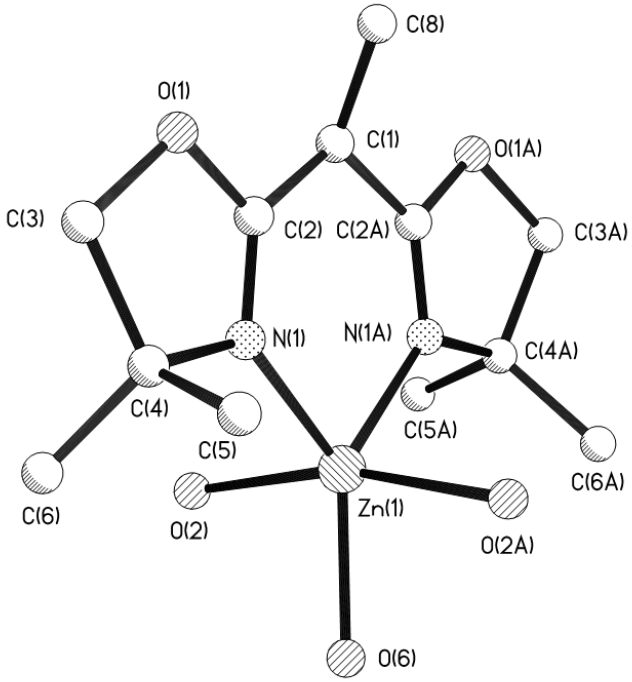

Figure S2. Molecular structure of the complex cation $[(Me_2BOX)Zn(H_2O)_3]^{2+}$ in **3a**. Principal bond lengths (Å) and angles (°): N(1)-Zn(1) 2.011(2), O(2)-Zn(1) 2.097(2), O(6)-Zn(1) 1.980(3); N(1)-Zn(1)-N(1A) 93.18(10), O(2)-Zn(1)-O(6) 82.69(7).

4) Kinetics of the Hydrolysis of TNP

The rate of hydrolysis of tris(4-nitrophenyl)phosphate (TNP) promoted by complex **2** in H_2O/EtOH (70/30) in the pH range 7.0-10.0 was measured under pseudo-first-order conditions. The reaction was monitored by following the increase in absorbance at 405.0 nm, corresponding to the appearance of the product 4-nitrophenolate (4-NP) at 25°C. The pH was maintained by using HEPES (pH 7.0-8.1), EPPS (pH 8.2-8.5), or CHES (pH 8.6-10.0) buffers. The pH values in 30% ethanol were corrected by subtracting 0.09 from all readings from the pH meter.[2] Ionic strength was maintained by $NaNO_3$ at 100 mM.

A typical experiment consisted of loading a UV-visible cell with 3 mL of a stock solution containing the appropriate buffer and $NaNO_3$, and 25 μL of a stock solution of complex (12 mM). The reaction was initiated by injecting 15 μL of a stock solution of TNP (1 mM in dry THF). The concentration of complex was varied (0.01 to 0.1 mM) with constant [TNP] (0.005 mM). Plots of A(405 nm) versus time showed first-order behaviour, and the exponential growths were fitted to the appropriate equation to give the observed rate constants, k_{obs} (s^{-1}). Second order rate constants k' ($M^{-1}.s^{-1}$) were derived as (k_{obs}(TNP) – k_0(TNP))/[total Zn^{II} complex]. The background reaction rate constant (no metal complex present) was measured at all pH values by loading the UV-visible cell with all of the reagents as described above with exception of the complex. Each experiment was repeated at least twice, and the values reported are an average of these measurements. A graph of k' values versus pH is shown in Figure S3.

[2] R. G. Bates, M. Paabo, R. A. Robinson, *J. Phys. Chem*. **1963**, *67*, 1883.

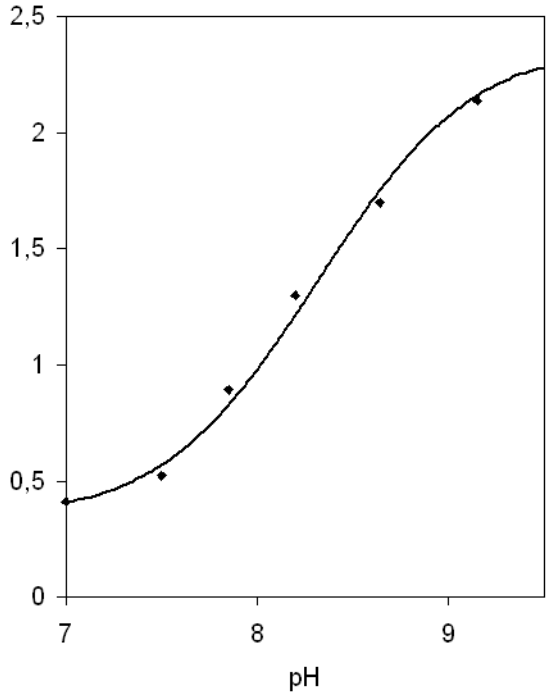

Figure S3. Dependence of *k'* on pH for the hydrolysis of TNP in EtOH/H_2O (30/70).