

Supporting Information

Structural Diversity of Alkylzinc Complexes with Pyrrole-Based N,O-Ligands: From Molecular Complexes to Coordination Polymers

Zbigniew Wróbel,^a Iwona Justyniak^a, Izabela Dranka,^b and Janusz Lewiński^{*a,b}

^a Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

^b Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland;

*E-mail: lewin@ch.pw.edu.pl

Contents:

1. General experimental procedures.....	S2
2. Synthesis of [EtZn(PyrC(O)OMe)] _n (1 _n).....	S2
3. Synthesis of [tBuZn(PyrC(O)OMe)] (2).....	S2
4. Synthesis of [EtZn(PyrC(O)H)] _n (3 _n).....	S3
5. Synthesis of [tBuZn(PyrC(O)H)] ₆ (4 ₆).....	S3
6. General comments on crystallographic data.....	S4

- 1. General experimental procedures:** All operations were carried out under dry nitrogen using standard Schlenk techniques. ${}^t\text{Bu}_2\text{Zn}^1$ was synthesized according to the literature method under a nitrogen atmosphere using standard Schlenk techniques. All other reagents were purchased from Sigma-Aldrich Co and use as received. Solvents were purified prior to use using MBraun solvent purification system MB SPS-800. ${}^1\text{H}$ NMR spectra were acquired on Varian Mercury 400 MHz spectrometer at 298 K. Chemical shifts are expressed in δ (ppm). The infrared spectra were recorded on an FT-IR Bruker TENSOR II spectrometer.
- 2. Synthesis of $[\text{EtZn}(\text{PyrC}(\text{O})\text{OMe})]_n$ ($\mathbf{1}_n$).** A solution of 1H-pyrrole-2-carboxaldehyde (0.1 g, 0,81 mmol) in toluene (5 ml) was cooled to -78°C , and Et_2Zn (0,405 ml of a 2 M solution in hexene, 0,81 mmol) was added dropwise. The reaction mixture was warmed to the room temperature and stirred for 4 h. Then, the mother solution was concentrated to 2 ml. Complex $\mathbf{1}_n$ was obtained as colorless needles like crystals after 24h from a toluene solution at room temperature. ${}^1\text{H}$ NMR (400MHz, CDCl_3): δ , ppm, 0,61 (q, 2H, ZnCH_2CH_3), 1,29 (t, 3H, ZnCH_2CH_3), 3,97 (s, 3H, CH_3), 6,39 (s, 1H, $\text{CH}_{\text{pyrrol}}$), 7,00 (d, 1H, $\text{CH}_{\text{pyrrol}}$), 7,06 (s, 1H, $\text{CH}_{\text{pyrrol}}$); IR (ATR) cm^{-1} : 3377 (w), 3112 (vw), 2953 (w), 2887 (w), 2853 (w), 2811 (vw), 2160 (vw), 2113 (vw), 1681 (w), 1600 (s), 1556 (w), 1505 (m), 1435 (s), 1402 (m), 1379 (s), 1354 (s), 1327 (m), 1308 (m), 1213 (m), 1187 (s), 1167 (s), 1129 (m), 1110 (m), 1081 (m), 1037 (s), 984 (s), 955 (m), 927 (m), 895 (m), 882 (m), 798 (m), 783 (m), 742 (vs), 640 (s), 628 (m), 609 (s), 545 (s), 533 (s), 460 (m), 438 (s), 430 (s), 422 (s), 412 (s), 405 (s). Elemental analysis: calcd. for $\text{C}_8\text{H}_{11}\text{NO}_2\text{Zn}$: % C 44,17 , % H 5,14; found % C 43,97 , % H 5,03
- 3. Synthesis of $[\text{}^t\text{BuZn}(\text{PyrC}(\text{O})\text{OMe})]$ ($\mathbf{2}$).** A solution of 1H-pyrrole-2-carboxaldehyde (0.1 g, 0,81 mmol) in hexane (5 ml) was cooled to -78°C , and ${}^t\text{Bu}_2\text{Zn}$ (0,81 ml of a 1 M solution in toluene, 0,81 mmol) was added dropwise. The reaction mixture was warmed to the room temperature and stirred for 4 h. ${}^1\text{H}$ NMR (400MHz, C_6D_6): δ , ppm, 1,29 (s, 9H, $\text{ZnC}(\text{CH}_3)_3$), 3,31 (s, 3H, CH_3), 6,46 (s, 1H, $\text{CH}_{\text{pyrrol}}$), 6,97 (s, 1H, $\text{CH}_{\text{pyrrol}}$), 7,20 (s, 1H, $\text{CH}_{\text{pyrrol}}$); IR (ATR) cm^{-1} : 3359 (vw), 3100 (vw), 2944 (vw), 2919 (vw), 2862 (vw), 2818 (w), 2757 (vw), 2697 (vw), 1650 (w), 1618 (w), 1595 (m), 1507 (m), 1434 (m), 1402 (w), 1378 (s), 1356 (s), 1310 (w), 1213 (m), 1204 (m), 1191 (m), 1167(m), 1112 (w), 1078 (w), 1038 (m), 1031(m), 991 (m), 940 (vw), 918 (vw), 897 (w), 883 (vw), 814 (w), 743(vs), 645 (w), 638 (w), 605(w), 537 (w), 502 (w), 437 (w), 424 (vw). Elemental analysis: calcd. for $\text{C}_{10}\text{H}_{15}\text{NO}_2\text{Zn}$: % C 49,02 , % H 6,17; found % C 48,73 , % H 6,09

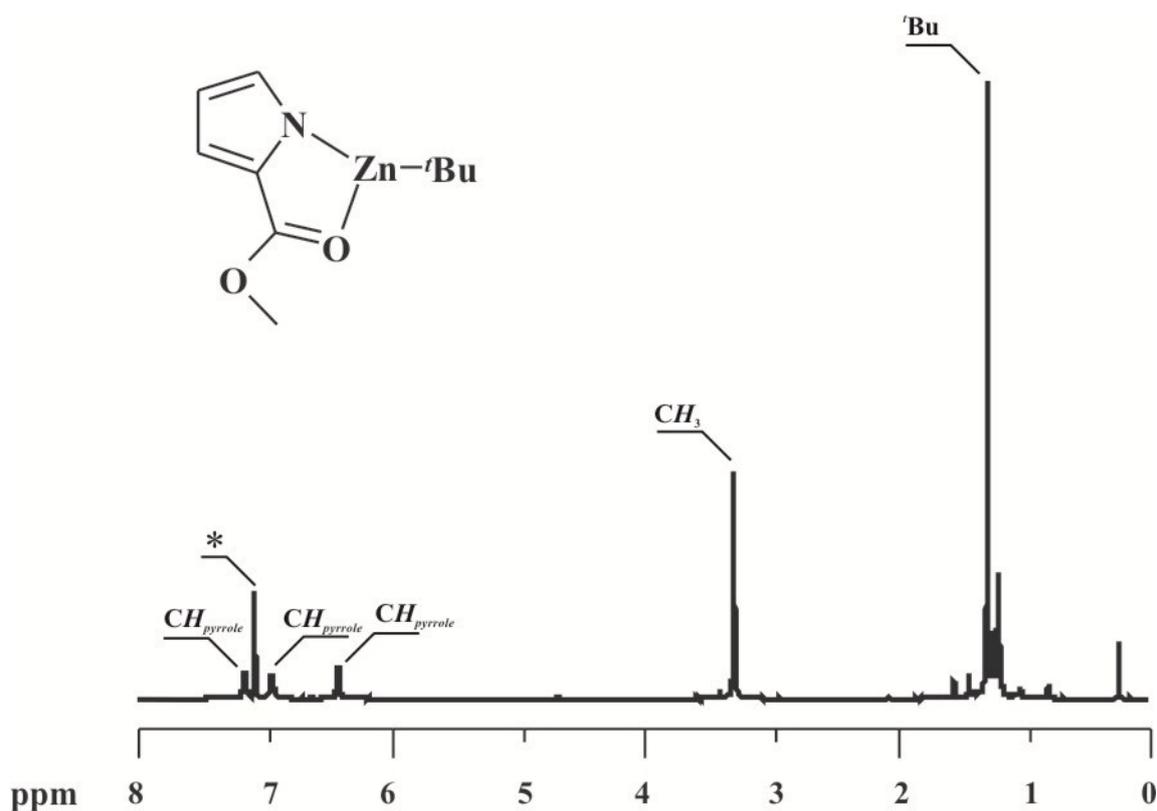


Figure S1. ^1H NMR spectrum of **2** (400 MHz, C_6D_6). * C_6D_6 .

- 4. Synthesis of $[\text{EtZn}(\text{PyrC}(\text{O})\text{H})]_n$ (**3_n**).** A solution of 1H-pyrrole-2-carboxaldehyde (0.115 g, 1,21 mmol) in toluene (5 ml) and THF (3 ml) was cooled to -78°C , and Et_2Zn (0.605 ml of a 2 M solution in hexene, 1,21 mmol) was added dropwise. The reaction mixture was warmed to the room temperature and stirred for 4 h. Then, the mother solution was concentrated to 5 ml. Complex **3_n** was obtained as colorless needles like crystals after 24h from a toluene solution at 5°C . ^1H NMR (400MHz, CDCl_3): δ , ppm, 0,85 (q, 2H, ZnCH_2CH_3), 1,25 (t, 3H, ZnCH_2CH_3), 6,37 (m, 1H, $\text{CH}_{\text{pyrrol}}$), 6,98 (m, 1H, $\text{CH}_{\text{pyrrol}}$), 7,12 (m, 1H, $\text{CH}_{\text{pyrrol}}$), 8,44 (s, 1H, $\text{CH}_{\text{carbonyl}}$); IR (ATR) cm^{-1} : 3383 (vw), 3091 (vw), 3026 (vw), 2925 (w), 2886 (w), 2848 (w), 2806 (w), 2359 (vw), 2151 (vw), 2052 (vw), 1987 (vw), 1946 (vw), 1759(vw), 1571 (vs), 1495 (w), 1443 (m), 1421 (m), 1385 (s), 1350 (m), 1310 (s), 1295 (s), 1273 (s), 1199 (s), 1082 (w), 1039 (vs), 987 (s), 974 (s), 951 (m), 918 (w), 889 (m), 868 (w), 794 (vs), 760 (vs), 733 (vs), 696 (s), 670 (m), 605 (m), 596 (s), 566 (s), 513 (s), 465 (s), 447 (m), 439 (m), 429 (m), 423 (m), 418 (m), 409 (m), 402 (m). Elemental analysis: calcd. for $\text{C}_7\text{H}_9\text{NOZn}$: % C 45,08 , % H 4,35; found % C 44,96 , % H 4,26
- 5. Synthesis of $[\text{tBuZn}(\text{PyrC}(\text{O})\text{H})]_6$ (**4₆**).** A solution of 1H-pyrrole-2-carboxaldehyde (0.133 g, 1,40 mmol) in toluene (4 ml) was cooled to -78°C , and tBu_2Zn (1,4 ml of a 1 M solution in toluene, 1,40 mmol) was added dropwise. The reaction mixture was warmed

to the room temperature and stirred for 4 h. Then, the mother solution was concentrated to 5 ml. Complex **4₆** was obtained as colorless needles like crystals after 24h from a toluene solution at 5°C. ¹H NMR (400MHz, C₆D₆): δ, ppm, 1,25 (s, 9H, ZnC(CH₃)₃), 6,48 (m, 1H, CH_{pyrrol}), 6,82 (m, 1H, CH_{pyrrol}), 7,05 (m, 1H, CH_{pyrrol}), 9,19 (s, 1H, CH_{carbonyl}); IR (ATR) cm⁻¹: 3368 (vw), 2947 (vw), 2919 (vw), 2862 (vw), 2817 (vw), 2697 (vw), 2115 (vw), 1682 (w), 1598 (m), 1557 (w) 1506 (m), 1436 (s), 1402 (w), 1379 (s), 1355 (s), 1327 (m), 1213 (m), 1188 (s), 1167 (s), 1130 (w), 1112 (w), 1081 (m), 1038 (m), 991 (m), 920 (w), 897 (w), 883 (w), 814 (w), 743(vs), 639 (w), 605 (w), 535 (m), 437 (w). Elemental analysis: calcd. for C₉H₁₃NOZn: % C 50,04 , % H 6,07; found % C 49,98 , % H 5,99

6. General comments on crystallographic data:

The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer² using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was mounted in a nylon loop in a drop of silicon oil to prevent the possibility of decay of the crystal during data collection. The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with *DENZO* and *SCALEPACK* (*HKL2000* package)³. The structure was solved by direct methods using the SHELXS97 program and was refined by full matrix least-squares on F² 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 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon.

¹ J. Lewiński, M. Dranka, W. Bury, W. Śliwiński, I. Justyniak, J. Lipkowski, *J. Am. Chem. Soc.*, 2007, **129**, 3096

² *KappaCCD Software*; Nonius B.V.: Delft, The Netherlands, **1998**.

³ Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, 276, 307.

⁴ G. M. Sheldrick, *Acta Cryst.* **2008**, 64A, 112-122.