New Events in Zinc Carboxylate Chemistry: Alkylzinc Carboxylates as Efficient Precursors for Zinc Oxocarboxylates and Sulfidocarboxylates

Janusz Lewiński, 1, a Wojciech Bury, 2 Michał Dutkiewicz, 1 Michał Maurin, 1 Iwona Justyniak, 2 and Janusz Lipkowski 2

1Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, PL-00-664 Warsaw, Poland
2Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warsaw, Poland

Figure S1. Molecular structure of 2 with thermal ellipsoids drawn at the 40% probability level; hydrogen atoms are omitted for clarity.
Figure S2. $^1$H NMR spectra for the oxygenation of 1 in toluene-$d_8$ at $0^\circ$C: before introduction of $O_2$ (a); during the reaction with $O_2$: 2 min. (b), 5 min. (c), 10 min. (d), 15 min. (e), 30 min. (f) and 24 h (g).
X-Ray structure determination

Crystal data for [EtZn(O₂CPh)₂]₄, C₉₅H₉₇Zn₂O₁₂: Mᵣ = 1293.24. The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer[1] using graphite monochromated MoKα radiation (λ = 0.71073 Å). 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. Crystal dimensions 0.42 × 0.36 × 0.18 mm², trigonal, space group R-3 (no. 148), a = 13.5154(6) Å, c = 54.4271(3) Å, U = 8609.5(7) Å³, Z = 6, F(000) = 3960, Dᵣ = 1.497 g m⁻³, μ(Mo-Kα) = 2.56 mm⁻¹, θ(max) = 27.48°, 4394 unique reflections. The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package)[2]. The structure was solved by direct methods using the SHELXS97[3] program and was refined by full matrix least-squares on F² using the program SHELXL97.[4] H-atoms were included in idealized positions and refined isotropically. Refinement converged at R₁ = 0.0308, wR₂ = 0.0725 for all data and 219 parameters (R₁ = 0.0283, wR₂ = 0.0711 for 4109 reflections with Iᵣ > 2σ(Iᵣ)). The goodness-of-fit on F² was equal 1.107. 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 = +0.84/-0.67 eÅ⁻³. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-653815. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for Zn₄(μ-L-O)(O₂CPh)₆, C₂₂H₁₆Zn₄O₁₈: M = 1004.25. The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer[1] using graphite monochromated MoKα radiation (λ = 0.71073 Å). The crystal was mounted in a nylon loop in an adrop of silicon oil to prevent the possibility of decay of the crystal during data collection crystal dimensions 0.56 × 0.38 × 0.32 mm³, cubic, space group I a-3d, a = 39.9595(5) Å, U = 63808.2(2) Å³, Z = 48, F(000) = 22320, Dᵣ = 1.158 g m⁻³, μ(Mo-Kα) = 1.83 mm⁻¹, θ(max) = 18.84°, 2092 unique reflections. The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package)[2]. The structure was solved by direct methods using the SHELXS97[3] program and was refined by full matrix least-squares on F² using the program SHELXL97.[4] H-atoms were included in idealized positions and refined isotropically. Refinement converged at R₁ = 0.0847, wR₂ = 0.2279 for all data and 173 parameters (R₁ = 0.0825, wR₂ = 0.2251 for 2019 reflections with Iᵣ > 2σ(Iᵣ)). The goodness-of-fit on F² was equal 1.074. 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 = +0.72/-0.35 eÅ⁻³. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-654048. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for [Zn₄(μ₃-μ-S)₂(O₂Ph)₆(THF)]₃, C₉₅H₉₇Zn₄S₂O₁₈C₄H₈O: M = 1641.80. The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer[1] using graphite monochromated MoKα radiation (λ = 0.71073 Å). The crystal was mounted in a nylon loop in an adrop of silicon oil to prevent the possibility of decay of the crystal during data collection crystal dimensions 0.48 × 0.32 × 0.22 mm³, triclinic, space group P -1 (no. 2), a = 10.5411(8) Å, b = 13.2402(9) Å, c = 13.4481(9) Å, α = 80.522(6)°, β = 74.576(6)°, γ = 82.868(4)°, U = 1778.0(3) Å³, Z = 1, F(000) = 876, Dᵣ = 1.60 g m⁻³, μ(Mo-Kα) = 2.12 mm⁻¹, θ(max) = 22.46°, 4611
unique reflections. The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package)[2]. 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 = 0.1007, wR2 = 0. 1153 for all data and 452 parameters (R1 = 0.0514, wR2 = 0. 1029 for 2919 reflections with I_o > 2σ(I_o)). The goodness-of-fit on F^2 was equal 1.053. A weighting scheme w = [σ(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 = +0.54/-0.57 eÅ^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 653816. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).