Supporting Information for

Di- and Tri-Zinc Catalysts for the Low Pressure Copolymerization of CO₂ and Cyclohexene Oxide

Michael R. Kember, Andrew J.P. White, Charlotte K. Williams* Department of Chemistry, Imperial College London, London, SW7 2AZ, UK. Corresponding author email address: c.k.williams@imperial.ac.uk

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X-ray crystallography

In the structure of $[L^1Zn_3(OAc)_4]$, disorder was found in the C(24) *tert*-butyl group. In each case two orientations were identified, of *ca*. 58 and 42% occupancy, with only the non-hydrogen atoms of the major occupancy orientation being refined anisotropically. The included toluene solvent was found to be distributed across two 50% occupancy sites, both adjacent to a centre of symmetry. In each case the solvent was disordered, and two complete partial occupancy orientations were identified of *ca*. 34:16 and 29:21% occupancy (with two further orientations related to these by the action of the centre of symmetry in each case), and they were each refined isotropically with idealised geometries. All four of the N–H protons were found from ΔF maps and refined subject to an N–H distance constraint of 0.90 Å.

The structure of $[L^2Zn_3(OAc)_4]$ was found to contain two crystallographically independent molecules, $[L^2Zn_3(OAc)_4]$ -I and $[L^2Zn_3(OAc)_4]$ -II shown in Figs. 4 and S4 respectively. Substantial disorder was found in the Zn(3) portion of the first independent molecule, involving also the O(45)/O(47) and O(50)/O(52) acetate moieties. Two separate orientations were identified, as shown in Fig. S3, of *ca*. 86 and 14% occupancy, with only the non-hydrogen atoms of the major occupancy orientation being refined anisotropically. The minor occupancy orientations of the two acetate moieties were restrained to have symmetric C–O distances, fixed C–C distances of 1.52 Å, and to be flat. The major occupancy orientation of the O(50)/O(52) acetate was also restrained to be flat.

The N–H protons could not be reliably located and so were placed in idealised positions with an N– H distance of 0.90 Å. The solvent present in the structure of $[L^2Zn_3(OAc)_4]^1$ was found to be highly disordered, and so the SQUEEZE procedure of the PLATON program was used, suggesting 589 electrons per unit cell, equivalent to *ca*. 74 electrons per complex. Before the use of SQUEEZE, the solvent had most resembled tetrahydrofuran (which has 40 electrons) in six different sites per asymmetric unit. The 74 electrons per complex suggested by SQUEEZE closely corresponds to 1.75 tetrahydrofuran molecules (70 electrons) per complex, so the contents of the unit cell were adjusted on the basis of this being the solvent present.

The crystals of $[L^3Zn_3(OAc)_4]$ were found to desolvate rapidly upon removal from the mother liquor, and the remaining fragments were very weakly diffracting. For this reason the resolution of the data collection was trimmed to 0.9 Å. The structure was found to contain three crystallographically independent molecules, $[L^3Zn_3(OAc)_4]$ -I, $[L^3Zn_3(OAc)_4]$ -II and $[L^3Zn_3(OAc)_4]$ -III, shown in Figs. 5, S7 and S9 respectively. Disorder was found in the O(31") methoxy unit of molecule III; two positions for the methyl group were identified, of *ca*. 53 and 47% occupancy, with only the major occupancy carbon atom being refined anisotropically. All twelve of the N–H protons were found from ΔF maps and refined subject to an N–H distance constraint of 0.90 Å. The solvent present in the structure of $[L^3Zn_3(OAc)_4]$ was found to be highly disordered, and so the SQUEEZE procedure of the PLATON program^[S1] was used, suggesting 537 electrons per unit cell, equivalent to *ca*. 90 electrons per complex. Before the use of SQUEEZE, the solvent had not been identified, so it was assumed to be the crystallisation solvent, tetrahydrofuran, which has 40 electrons per molecule. The 90 electrons per complex suggested by SQUEEZE closely corresponds to 2.25 tetrahydrofuran molecules (90 electrons) per complex, so the contents of the unit cell were adjusted on the basis of this being the solvent present.



Fig. S1The molecular structure of $[L^1Zn_3(OAc)_4]$ (30% probability ellipsoids).

Table S1.	Selected bond lengths (Å) and angles (°) for $[L^1Zn_3(OAc)_4]$.

Zn(1)-O(1)	2.2843(14)	Zn(1)-N(4)	2.1284(17)
Zn(1)-N(8)	2.0923(17)	Zn(1)-O(11)	2.0587(14)
Zn(1)–O(40)	2.1491(15)	Zn(1)–O(45)	2.1309(15)
Zn(2)-O(1)	2.2027(14)	Zn(2)-O(11)	2.1003(13)
Zn(2)-N(14)	2.1286(18)	Zn(2) - N(18)	2.1320(17)
Zn(2)–O(42)	2.0873(15)	Zn(2)–O(50)	2.1112(15)
Zn(3)-O(1)	1.9884(14)	Zn(3)–O(45)	2.0244(15)
Zn(3)–O(52)	1.9354(18)	Zn(3)–O(55)	1.9521(18)
Zn(3)–O(57)	2.576(2)	O(1)-C(1)	1.367(2)
O(11)–C(11)	1.348(2)		
O(1)-Zn(1)-N(4)	90.03(6)	O(1) - Zn(1) - N(8)	174.77(6)
O(1)-Zn(1)-O(11)	82.21(5)	O(1)-Zn(1)-O(40)	90.33(5)
O(1)-Zn(1)-O(45)	76.37(5)	N(4) - Zn(1) - N(8)	91.25(6)
N(4)-Zn(1)-O(11)	169.89(6)	N(4) - Zn(1) - O(40)	80.64(6)
N(4)-Zn(1)-O(45)	93.18(7)	N(8)-Zn(1)-O(11)	95.92(6)
N(8)-Zn(1)-O(40)	84.88(6)	N(8)-Zn(1)-O(45)	108.61(6)
O(11)-Zn(1)-O(40)	92.89(6)	O(11)-Zn(1)-O(45)	91.27(6)
O(40)-Zn(1)-O(45)	165.40(6)	O(1)-Zn(2)-O(11)	83.28(5)
O(1)-Zn(2)-N(14)	176.26(6)	O(1)-Zn(2)-N(18)	91.34(6)
O(1)-Zn(2)-O(42)	93.40(6)	O(1)-Zn(2)-O(50)	90.54(6)
O(11)-Zn(2)-N(14)	93.56(6)	O(11)-Zn(2)-N(18)	173.99(6)
O(11)-Zn(2)-O(42)	94.53(6)	O(11)-Zn(2)-O(50)	94.04(6)
N(14)-Zn(2)-N(18)	91.91(7)	N(14)-Zn(2)-O(42)	88.84(7)
N(14)-Zn(2)-O(50)	87.68(7)	N(18)–Zn(2)–O(42)	83.07(6)
N(18)–Zn(2)–O(50)	88.68(6)	O(42)–Zn(2)–O(50)	170.93(6)
O(1)–Zn(3)–O(45)	85.82(6)	O(1)–Zn(3)–O(52)	118.16(6)
O(1)–Zn(3)–O(55)	115.43(7)	O(45)–Zn(3)–O(52)	105.10(7)
O(45)–Zn(3)–O(55)	101.87(7)	O(52)–Zn(3)–O(55)	120.84(8)



Fig. S2 The molecular structure of one $([L^2Zn_3(OAc)_4]-I)$ of the two crystallographically independent complexes present in the crystals of $[L^2Zn_3(OAc)_4]$ (30% probability ellipsoids).



Fig. S3 The molecular structure of one $([L^2Zn_3(OAc)_4]-I)$ of the two crystallographically independent complexes present in the crystals of $[L^2Zn_3(OAc)_4]$ showing the disorder in the Zn(3) unit. The major occupancy orientation (*ca.* 86%) has been drawn with line bonds, and the minor (*ca.* 14%) with dashed bonds.



Fig. S4 The molecular structure of one $([L^2Zn_3(OAc)_4]$ -II) of the two crystallographically independent complexes present in the crystals of $[L^2Zn_3(OAc)_4]$.



Fig. S5 The molecular structure of one $([L^2Zn_3(OAc)_4]$ -**II**) of the two crystallographically independent complexes present in the crystals of $[L^2Zn_3(OAc)_4]$ (30% probability ellipsoids).

Table S2. Selected bond lengths (Å) and angles (°) for the two independent molecules (I and II)present in the crystals of $[L^2Zn_3(OAc)_4]$.

	Ι	II		Ι	Π
Zn(1)-O(1)	2.232(3)	2.314(2)	Zn(2)–O(42)	2.104(3)	2.131(3)
Zn(1)-N(4)	2.106(3)	2.126(4)	Zn(2)–O(50)	2.164(3)	2.109(3)
Zn(1) - N(8)	2.074(3)	2.099(3)	Zn(3)-O(1)	1.974(3)	2.013(2)
Zn(1)–O(11)	2.093(3)	2.050(3)	Zn(3)–O(45)	2.012(4)	n/a
Zn(1)–O(45)	2.177(3)	2.142(3)	Zn(3)–O(47)	n/a	1.964(3)
Zn(1)-O(40)	2.125(3)	2.101(3)	Zn(3)–O(52)	1.955(3)	1.934(3)
Zn(2)-O(1)	2.215(3)	2.253(2)	Zn(3)–O(55)	2.034(3)	1.933(3)
Zn(2)–O(11)	2.054(3)	2.068(2)	Zn(3)–O(57)	2.361(4)	3.025(4)
Zn(2)–N(14)	2.119(3)	2.112(3)	O(1)-C(1)	1.373(4)	1.364(5)
Zn(2)–N(18)	2.120(3)	2.130(3)	O(11)–C(11)	1.351(4)	1.347(4)
O(1) - Zn(1) - N(4)	92.43(12)	90.44(11)	N(14)–Zn(2)–	93.67(13)	93.48(11)
O(1) - Zn(1) - N(8)	171.92(1	174.13(1	O(11) - Zn(2) -	94.67(11)	95.54(10)
O(1)–Zn(1)–O(11)	78.96(10)	80.45(9)	O(42) - Zn(2) -	168.10(1	169.05(1
O(1)–Zn(1)–O(40)	93.81(10)	92.59(10)	N(14)-Zn(2)-	87.34(12)	86.18(12)
O(1)–Zn(1)–O(45)	75.92(13)	90.48(10)	N(18) - Zn(2) -	86.36(12)	87.96(11)
N(4)-Zn(1)-N(8)	95.11(13)	94.07(13)	O(11)-Zn(2)-O(1)	80.19(10)	81.53(9)
N(4)–Zn(1)–O(11)	171.08(1	170.54(1	O(42)-Zn(2)-O(1)	95.57(11)	93.29(10)
N(4)-Zn(1)-O(40)	83.99(13)	82.25(12)	N(14)-Zn(2)-O(1)	174.92(1	174.46(1
N(4)–Zn(1)–O(45)	91.79(14)	89.27(14)	N(18)-Zn(2)-O(1)	90.85(11)	90.91(10)
N(8)–Zn(1)–O(11)	93.61(11)	95.20(11)	O(50)-Zn(2)-O(1)	90.63(11)	90.61(10)
N(8)–Zn(1)–O(40)	89.86(12)	91.75(12)	O(1)-Zn(3)-O(45)	85.74(13)	n/a
N(8)–Zn(1)–O(45)	100.91(1	85.82(12)	O(1)-Zn(3)-O(47)	n/a	118.45(10)
O(11)–Zn(1)–	94.17(11)	95.56(10)	O(1)-Zn(3)-O(52)	121.94(1	114.71(1
O(11)–Zn(1)–	88.39(12)	93.29(12)	O(1)-Zn(3)-O(55)	122.23(1	103.32(1
O(40)–Zn(1)–	168.75(1	171.00(1	O(45)–Zn(3)–	111.76(1	n/a
O(11)–Zn(2)–	96.39(11)	95.16(10)	O(45)–Zn(3)–	97.10(14)	n/a
O(11)–Zn(2)–	95.33(12)	94.28(11)	O(47)–Zn(3)–	n/a	99.68(14)
O(42)–Zn(2)–	87.28(12)	90.68(11)	O(47)–Zn(3)–	n/a	97.44(13)
O(11)–Zn(2)–	170.99(1	171.68(1	O(52)–Zn(3)–	110.31(1	122.94(1
O(42)–Zn(2)–	83.41(12)	81.76(11)			



Fig. S6 The molecular structure of one $([L^3Zn_3(OAc)_4]-I)$ of the three crystallographically independent complexes present in the crystals of $[L^3Zn_3(OAc)_4]$ (30% probability ellipsoids).



Fig. S7 The molecular structure of one $([L^3Zn_3(OAc)_4]$ -**II**) of the three crystallographically independent complexes present in the crystals of $[L^3Zn_3(OAc)_4]$.



Fig. S8 The molecular structure of one $([L^3Zn_3(OAc)_4]$ -**II**) of the three crystallographically independent complexes present in the crystals of $[L^3Zn_3(OAc)_4]$ (30% probability ellipsoids).



Fig. S9 The molecular structure of one $([L^3Zn_3(OAc)_4]$ -**III**) of the three crystallographically independent complexes present in the crystals of $[L^3Zn_3(OAc)_4]$.



Fig. S10 The molecular structure of one $([L^3Zn_3(OAc)_4]$ -**III**) of the three crystallographically independent complexes present in the crystals of $[L^3Zn_3(OAc)_4]$ (30% probability ellipsoids).

	Ι	II	III		Ι	II	III
Zn(1)-O(1)	2.284(2)	2.267(3)	2.284(3)	Zn(2)–O(42)	2.100(3)	2.106(3)	2.100(3)
Zn(1) - N(4)	2.126(3)	2.074(4)	2.123(4)	Zn(2)–O(50)	2.187(3)	2.207(3)	2.189(3)
Zn(1) - N(8)	2.092(3)	2.076(3)	2.073(3)	Zn(3)-O(1)	1.981(3)	2.010(3)	1.975(2)
Zn(1)-O(11)	2.066(3)	2.057(3)	2.066(3)	Zn(3)–O(45)	2.035(3)	2.003(3)	2.001(3)
Zn(1)-O(40)	2.133(3)	2.095(3)	2.100(3)	Zn(3)–O(52)	1.936(3)	1.929(3)	1.940(3)
Zn(1)-O(45)	2.162(3)	2.281(3)	2.279(3)	Zn(3)–O(55)	1.934(3)	1.932(3)	1.919(3)
Zn(2)-O(1)	2.245(3)	2.183(3)	2.228(3)	Zn(3)–O(57)	2.640(3)	2.717(3)	2.804(3)
Zn(2)-O(11)	2.092(3)	2.087(3)	2.102(3)	O(1) - C(1)	1.369(4)	1.370(4)	1.375(4)
Zn(2) - N(14)	2.106(4)	2.106(3)	2.098(4)	O(11)–C(11)	1.351(5)	1.360(4)	1.357(5)
Zn(2)–N(18)	2.106(3)	2.100(3)	2.115(4)				
O(1) - Zn(1) - N(4)	91.29(11)	91.20(12)	90.79(12)	O(1)–Zn(2)–O(42)	94.52(11)	98.30(11)	94.92(10)
O(1)-Zn(1)-N(8)	175.41(13)	168.34(12)	174.68(12)	O(1)-Zn(2)-O(50)	88.66(10)	91.03(11)	89.59(10)
O(1)-Zn(1)-O(11)	80.68(9)	76.34(10)	79.12(10)	O(11)–Zn(2)–N(14)	94.10(12)	94.17(12)	94.01(13)
O(1)-Zn(1)-O(40)	90.43(10)	96.85(11)	91.36(10)	O(11)–Zn(2)–N(18)	172.08(12)	169.52(12)	171.05(12)
O(1)-Zn(1)-O(45)	75.73(10)	75.96(10)	74.46(9)	O(11)–Zn(2)–O(42)	95.46(11)	95.16(11)	95.76(11)
N(4)-Zn(1)-N(8)	91.41(13)	97.59(14)	94.09(14)	O(11)–Zn(2)–O(50)	93.24(10)	93.76(11)	94.40(10)
N(4)-Zn(1)-O(11)	170.84(11)	167.46(13)	169.84(12)	N(14)-Zn(2)-N(18)	93.66(13)	96.31(13)	94.92(14)
N(4)-Zn(1)-O(40)	81.50(13)	84.37(15)	82.09(13)	N(14)-Zn(2)-O(42)	90.94(13)	85.25(14)	90.02(12)
N(4)-Zn(1)-O(45)	91.16(13)	91.98(15)	88.80(12)	N(14)-Zn(2)-O(50)	86.58(12)	86.53(14)	86.54(12)
N(8)-Zn(1)-O(11)	96.33(12)	94.95(12)	96.04(13)	N(18)-Zn(2)-O(42)	82.85(12)	85.53(13)	83.75(12)
N(8)–Zn(1)–O(40)	86.30(13)	91.65(13)	91.42(12)	N(18)-Zn(2)-O(50)	88.78(12)	87.09(13)	86.63(12)
N(8)-Zn(1)-O(45)	107.93(13)	96.00(12)	103.49(12)	O(42)–Zn(2)–O(50)	171.10(11)	168.27(11)	169.47(11)
O(11)-Zn(1)-O(40)	94.09(11)	95.66(11)	96.82(11)	O(1)–Zn(3)–O(45)	85.65(11)	88.46(12)	87.92(10)
O(11)-Zn(1)-O(45)	91.11(11)	86.33(11)	89.63(10)	O(1)–Zn(3)–O(52)	120.87(12)	121.44(12)	121.35(12)
O(40)-Zn(1)- $O(45)$	164.23(10)	171.91(11)	163.07(11)	O(1)–Zn(3)–O(55)	119.45(12)	120.21(13)	120.00(12)
O(1)-Zn(2)-O(11)	81.09(10)	77.60(10)	79.66(10)	O(45)-Zn(3)-O(52)	101.33(12)	108.00(14)	104.88(12)
O(1)-Zn(2)-N(14)	173.03(12)	171.26(11)	172.32(12)	O(45)–Zn(3)–O(55)	106.38(13)	100.66(13)	109.80(12)
O(1)-Zn(2)-N(18)	91.31(11)	91.94(11)	91.47(12)	O(52)–Zn(3)–O(55)	114.45(13)	111.40(15)	108.87(13)

Table S3. Selected bond lengths (Å) and angles (°) for the three independent molecules (I, II andIII) present in the crystals of $[L^3Zn_3(OAc)_4]$.



Figure S11: ¹H NMR spectra of $[L^2Zn_2(OAc)_2]$ at 110 °C in d²-TCE.



Figure S12: ¹H NMR spectra of $[L^{1}Zn_{3}(OAc)_{4}]$ at 25 °C in d⁴-methanol. Starred peak at 4.9 ppm corresponds to water present in the NMR solvent (3.31 ppm).



correspond to two separate acetate binding modes.



Fig. S14. ¹H NMR spectrum of poly(cyclohexene carbonate). Peak A (d = 4.65) is assigned to the polycarbonate linkages, peaks B (4.45 and 3.60) are assigned to the methyne groups on the end group (OCHC₄H₈CHOH),² peak C (d = 4.16 – 4.10) is assigned to the methyne groups on the cyclohexanol/cyclopentanol end groups, peak D is assigned to the *trans*-cyclic carbonate species.³ The absence of polyether resonances is confirmed by the lack of a signal at 3.45 ppm.

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