

Supporting information

From ethylzinc guanidinate to [Zn₁₀O₄]-supertetrahedron

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1. Synthesis and characterisation details

General remarks: All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen, using standard Schlenk and glove-box techniques unless noted otherwise. [EtZn(hpp)]₃ (**13**) was prepared according to the literature procedure.¹ All chemicals and solvents were purchased from Sigma-Aldrich. Solution of water in THF was prepared using deionised water, which was deoxygenated by vacuum treatment upon sonication followed by bubbling of N₂. Solvents were carefully dried and distilled immediately prior to use. NMR spectra were acquired using the Varian Mercury 400 MHz and Bruker Avance II 500 MHz spectrometers. PXRD measurement was performed using PANalytical Empyrean diffractometer equipped with Ni-filtered Cu K α radiation (40 kV, 40 mA). Samples for the PXRD analysis were sealed between two layers of polymer foil and measured in transmission geometry.

Synthesis of [Et₄Zn₁₀O₄(hpp)₈] (2**):** A THF solution of **13** (418 mg, 0.6 mmol) was cooled to -78 °C and afterwards a 1M solution of H₂O (0.24 ml, 0.24 mmol) in THF was added dropwise. The reaction mixture was slowly heated to room temperature and stirred overnight, which resulted in formation of a white precipitate. Filtration and washing of the precipitate with hexane followed by drying *in vacuo* resulted in formation of **2** as a white crystalline powder (216 mg, 62 %, reported yield is an average of several synthetic attempts). Single crystals of **2** were obtained by slightly modified procedure: After addition of water to the reaction mixture and reaching room temperature the stirring was disabled and the reaction mixture was kept still at room temperature for 48 h which resulted in formation of colourless single crystals of **2**. Phase analysis by PXRD revealed that both the single crystals and the white precipitate obtained by the presented methods were consisting of the same crystalline phase (Fig. S1). C, H, N (%) analysis of **2**: calculated for C₆₄H₁₁₆N₂₄O₄Zn₁₀: C 39.63, H 5.99, N 17.34; found: C 39.91, H

6.10, N 17.06. Due to extremely low solubility of **2** in common laboratory solvents the standard ^1H NMR characterisation was not feasible. Instead, ^{13}C and ^{15}N CPMAS NMR spectra were recorded in order to characterise the resulting compound in solid state. The asymmetric unit within the crystal structure of **2** comprises two monoanionic hpp ligands, which resulted in formation of broadened or separate signals of some ^{13}C and ^{15}N nuclei. ^{13}C CPMAS NMR: $\delta = 161.32$ and 159.27 ($\text{C}(-\text{N})_3$), $50.88 - 48.80$ ($\text{CH}_2-\text{CH}_2-\text{N}$), $46.79 - 43.48$ ($\text{CH}_2-\text{CH}_2-\text{N}$), 25.26 (br, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 15.03 ($\text{Zn}-\text{CH}_2-\text{CH}_3$), 0.81 ($\text{Zn}-\text{CH}_2-\text{CH}_3$) ppm. ^{15}N CPMAS NMR: $\delta = -265.50 - -286.28$ ($\text{Zn}-\text{N}$), -307.75 and -311.22 ($\text{N}(-\text{C})_3$) ppm.

Synthesis of $[\text{Zn}(\text{hpp})_2(\text{Ph}_2\text{CH}_3\text{CO})_2]$ (3**):** A suspension of **2** (97 mg, 0.05 mmol) in THF was cooled to $-20\text{ }^\circ\text{C}$ and the solution of 1,1-diphenylethanol ($\text{Ph}_2\text{CH}_3\text{COH}$) (40 mg, 0.2 mmol) in THF was added dropwise. The reaction mixture was heated to room temperature and stirred overnight. The obtained cloudy mixture was afterwards filtered and the resulting clear solution was concentrated and stored at $-20\text{ }^\circ\text{C}$ for crystallisation. After *ca.* one week colourless single crystals of **3** were collected, washed with hexane and dried (30 mg, 41%, calculated with regard to $\text{Ph}_2\text{CH}_3\text{COH}$). C, H, N (%) analysis of **3**: calculated for $\text{C}_{42}\text{H}_{52}\text{N}_6\text{O}_2\text{Zn}$: C 68.35, H 7.05, N 11.39; found: C 68.81, H 6.93, N 11.07. ^1H NMR (C_6D_6 , $25\text{ }^\circ\text{C}$): $\delta = 7.61$ (Ar-H, 8H), 7.18 (Ar-H, 8H), 7.07 (Ar-H, 4H), 2.59 ($\text{CH}_2-\text{CH}_2-\text{N}$, 8H), 2.26 ($\text{CH}_2-\text{CH}_2-\text{N}$, 8H), 2.11 (CH_3-Ar , 6H), 1.39 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$, 8H).

Reaction of **2 with Mes_2BOH :** A suspension of **2** (97 mg, 0.05 mmol) in THF was cooled to $-20\text{ }^\circ\text{C}$ and the solution of Mes_2BOH (53 mg, 0.2 mmol) in THF was added dropwise. The reaction mixture was heated to room temperature and stirred overnight. Despite several attempts of crystallisation of the product using various solvents and crystallisation conditions no single

crystals were obtained. ^1H NMR of the obtained mixture did not contain signals characteristic for ethylzinc groups and indicated formation of a complex mixture of products.

Reaction of $\mathbf{13}$ with $\text{Ph}_2\text{CH}_3\text{COH}$: A THF solution of $\mathbf{13}$ (209 mg, 0.3 mmol) was cooled to $-20\text{ }^\circ\text{C}$ and the solution of 1,1-diphenylethanol ($\text{Ph}_2\text{CH}_3\text{COH}$) (60 mg, 0.3 mmol) in THF was added dropwise. The reaction mixture was heated to room temperature and stirred overnight. Upon removal of solvent *in vacuo* a colourless gel-like solid was obtained. Alternatively the product could be precipitated using an excess of hexane, which resulted in formation of a white solid. PXRD analysis of the dried product revealed that it was amorphous (Figure S2).

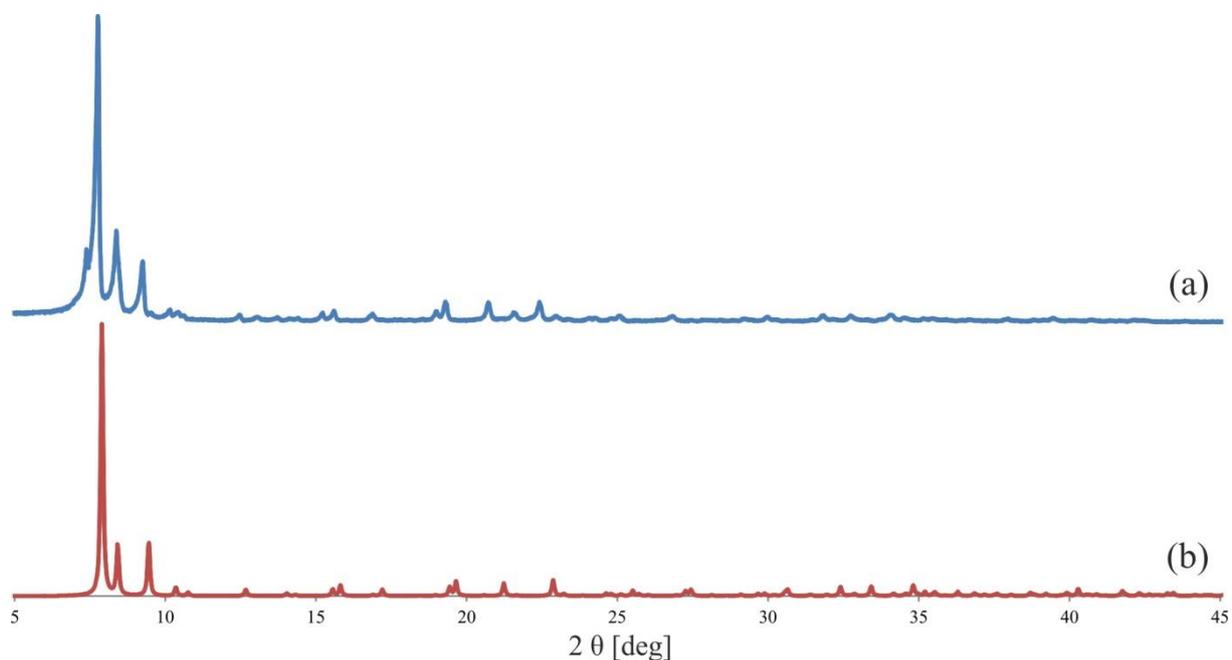


Figure S1. PXRD diffractograms of: precipitate of **2** formed according to the synthesis procedure (a) and simulated PXRD pattern based on the single crystal data of **2** (b).

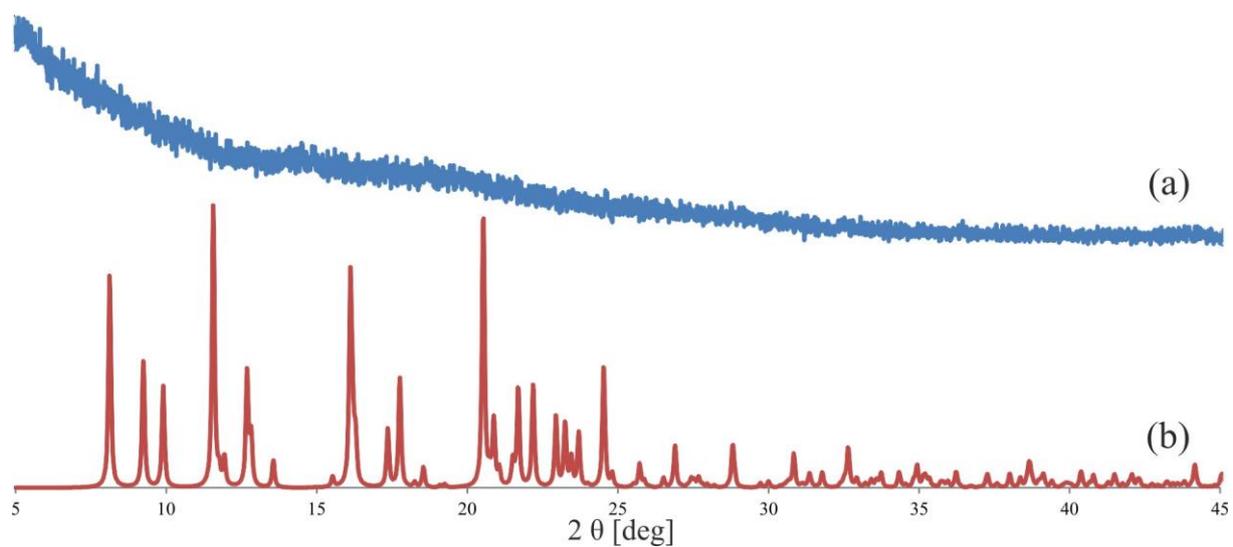


Figure S2. PXRD diffractograms of: solid product of the reaction between **1** and $\text{Ph}_2\text{CH}_3\text{COH}$ (a) and simulated PXRD pattern based on the single crystal data of **3** (b).

2. Crystallographic study of complexes **2** and **3**

The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for complexes **2** and **3** were collected at 100(2)K on a Nonius KappaCCD diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were processed with HKL2000.² The structure was solved by direct methods using the SHELXS-97 program and was refined by full matrix least-squares on F^2 using the program SHELXL-97.³ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

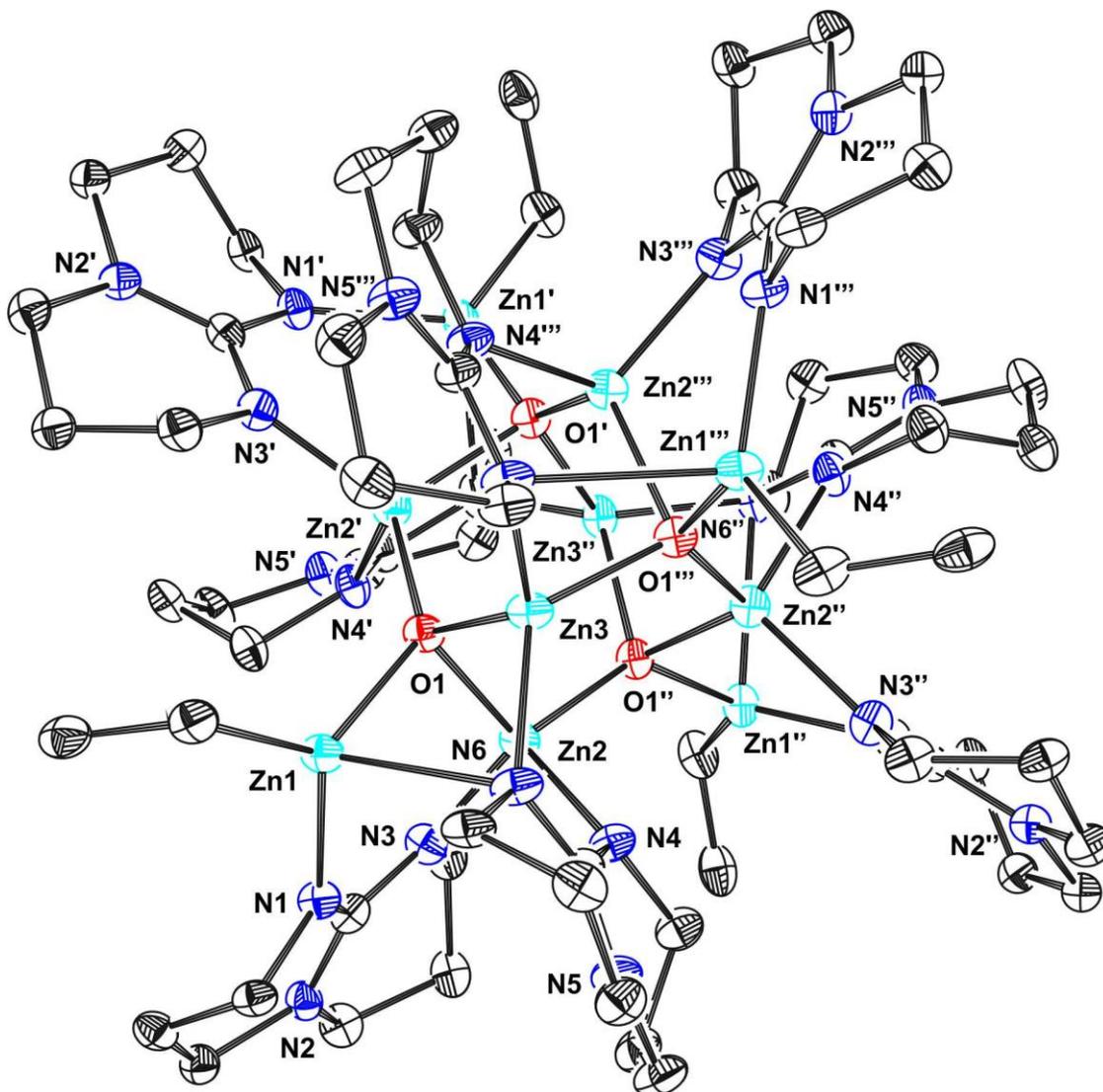


Figure S3. Molecular structure of **2** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Symmetry codes: $(-x+1/2, -y+1/2, z)$, $(y, -x+1/2, -z+1/2)$, $(-y+1/2, x, -z+1/2)$

Crystal data for **2**; $C_{64}H_{116}N_{24}O_4Zn_{10}$: $M = 1939.50$, crystal dimensions $0.36 \times 0.25 \times 0.10 \text{ mm}^3$, tetragonal, space group $P 42/n$ (no. 86), $a = 13.2190(4) \text{ \AA}$, $b = 13.2190(4) \text{ \AA}$, $c = 20.9750(5) \text{ \AA}$, $U = 3665.2(2) \text{ \AA}^3$, $Z = 2$, $F(000) = 2000$, $D_c = 1.757 \text{ g cm}^{-3}$, $K, \mu(\text{Mo-K}\alpha) = 3.275 \text{ mm}^{-1}$, $\theta_{\text{max}} = 27.483^\circ$, 4194 unique reflections, $R1 = 0.0942$, $wR2 = 0.1522$ for all data and 232 parameters and 0 restraints, $R1 = 0.0588$, $wR2 = 0.1358$ for 2960 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 1.079. 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 = $+0.86 / -0.65 \text{ e\AA}^{-3}$. **CCDC – 1545171.**

Table S1. Selected bonds and angles in the molecular structure of **2**.

2					
Bond lengths [Å]		Bond angles [°]			
Zn1-O1	1.959(4)	Zn1-O1-Zn2	96.71(15)	O1-Zn2-N3	112.23(19)
Zn1-N1	1.999(5)	Zn1-O1-Zn2'	132.88(19)	O1'-Zn2-N3	116.70(19)
Zn2-O1	1.983(4)	Zn1-O1-Zn3	94.91(17)	O1-Zn2-N4	104.07(16)
Zn2-O1'	1.937(4)	Zn2-O1-Zn2'	105.02(19)	O1'-Zn2-N4	106.28(18)
Zn2-N3	1.963(5)	Zn2-O1-Zn3	100.04(15)	N3-Zn2-N4	105.4(2)
Zn2-N4	2.040(5)	Zn2-O1-Zn3'	120.90(18)	O1-Zn3-O1'	105.06(16)
Zn3-O1	1.983(4)	O1-Zn1-N1	112.61(19)	O1-Zn3-N6	124.94(17)
Zn3-N6	2.026(5)	O1-Zn1-N6	79.94(16)	O1-Zn3-N6'	93.95(17)
		O1-Zn2-O1'	111.09(15)	N6-Zn3-N6	116.4(2)

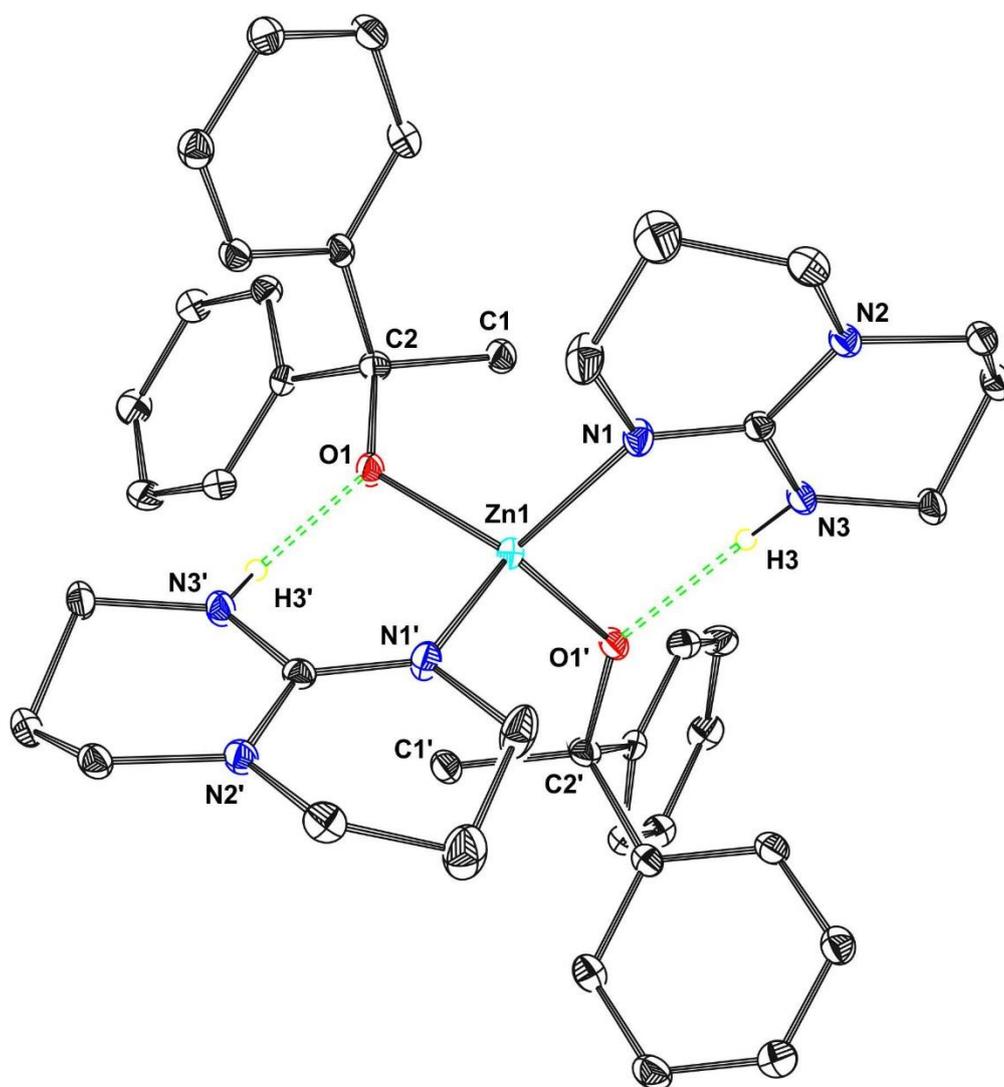


Figure S4. Molecular structure of **3** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Symmetry codes: $(-x, y, -z+1/2)$

Crystal data for **3**; C₄₂H₅₂N₆O₂Zn: $M = 738.26$, crystal dimensions $0.28 \times 0.20 \times 0.10 \text{ mm}^3$, monoclinic, space group P 2/c (no. 13), $a = 14.0610(8) \text{ \AA}$, $b = 8.9270(3) \text{ \AA}$, $c = 19.1620(9) \text{ \AA}$, $\beta = 129.338(2)^\circ$, $U = 1860.28(16) \text{ \AA}^3$, $Z = 2$, $F(000) = 784$, $D_c = 1.318 \text{ g cm}^{-3}$, $K, \mu(\text{Mo-K}\alpha) = 0.705 \text{ mm}^{-1}$, $\theta_{\text{max}} = 25.992^\circ$, 3623 unique reflections, $R1 = 0.0632$, $wR2 = 0.1255$ for all data and 232 parameters and 0 restraints, $R1 = 0.0518$, $wR2 = 0.1181$ for 3158 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 1.074. 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 = $+ 1.48 / -0.53 \text{ e\AA}^{-3}$. **CCDC – 1545172.**

Table S2. Selected bonds and angles in the molecular structure of **3**.

3					
Bond lengths [Å]		Bond angles [°]			
Zn1-O1	1.9305(17)	O1-Zn1-O1'	115.44(9)	N1-Zn1-N1'	106.56(13)
Zn1-N1	2.017(4)	O1-Zn1-N1	114.92(11)	N3-H3-O1	155.8(2)
H3-O1	1.849(3)	O1-Zn1-N1'	102.55(10)		

3. References

- 1 K. Zelga, M. Leszczyński, I. Justyniak, A. Kornowicz, M. Cabaj, A. E. H. Wheatley and J. Lewiński, *Dalton Trans.*, 2012, **41**, 5934.
- 2 *KappaCCD Software*; Nonius B.V.: Delft, The Netherlands, 1998.
- 3 G. M. Sheldrick, *Acta Cryst.* 2008, **64A**, 112.