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# Poly[[$\mu_4$-4-(carboxylatomethyl)benzoato]zinc(II)]

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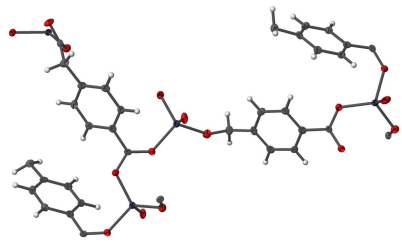
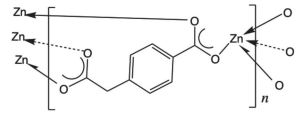
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title compound, $[Zn(C_9H_6O_4)]_n$, the $Zn^{II}$ cations are coordinated in a tetrahedral fashion by carboxylate O-atom donors belonging to four 4-(carboxymethyl) benzoate (4-cmb) ligands. Each 4-cmb ligand binds to four $Zn^{II}$ cations in an exotetradentate fashion to create a non-interpenetrated $[Zn(4\text{-cmb})]_n$ three-dimensional coordination polymer network with a new non-diamondoid $6^6$ topology. The crystal studied was refined as an inversion twin.

**3D view**



**Chemical scheme**




## Structure description

The title compound was isolated during an exploratory synthetic effort aiming to produce a zinc coordination polymer containing both 4-(carboxymethyl)benzoate (4-cmb) and bis(4-pyridyl)urea (bpu) ligands. The bpu ligand has seldom been used in coordination polymer chemistry to date (Kumar *et al.*, 2007).

The asymmetric unit of the title compound contains a single $Zn^{II}$ cation and a single deprotonated 4-cmb ligand. The divalent Zn atom is coordinated in a distorted tetrahedral fashion, with single carboxylate O-atom donors from four different 4-cmb ligands comprising the coordination environment (Fig. 1).

The 4-cmb ligands in the title compound adopt an exotetradentate $\mu_4$-$\kappa^4$-*O*:*O*′:*O*″:*O*‴ bridging mode (Fig. 2). The shorter carboxylate arms of the 4-cmb ligands construct $[Zn(OCO)]_n$ chain motifs parallel to the *a* axis, with an *anti–syn* bridging mode and a Zn···Zn internuclear distance of 4.875 (1) Å. Meanwhile, the longer carboxylate arms of the 4-cmb ligands construct $[Zn(OCO)]_n$ chain motifs parallel to the *b* axis, also with an *anti–syn* bridging mode. The Zn···Zn distance in this case measures 4.861 (1) Å, which matches the *b* lattice parameter. The full span of the 4-cmb ligands constructs a non-interpenetrated three-dimensional $[Zn(4\text{-cmb})]_n$ coordination polymer network (Fig. 3). The topology of the title complex can be simplified by considering both the Zn atoms and the exotetradentate 4-cmb ligands as 4-connected nodes. A topological analysis performed with *TOPOS* software (Blatov *et al.*, 2014) reveals the presence of a new

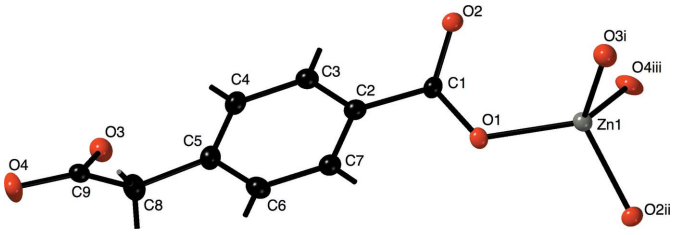



**Figure 1**
The distorted tetrahedral coordination environment of zinc(II) in the title compound. Displacement ellipsoids are drawn at the 50% probability level. H-atom positions are shown as sticks.

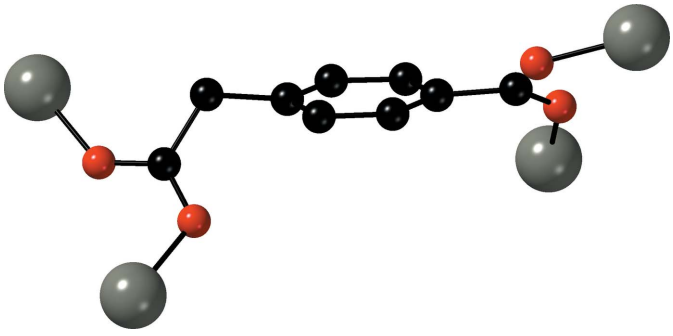


**Figure 2**
The exotetradentate $\mu_4$-$\kappa^4$-*O*:*O*′:*O*″:*O*‴ bridging mode of the 4-cmb ligand in the title compound. Color code: Zn, gray, O, red; C, black.

underlying non-diamondoid $6^6$ topology (Fig. 4). While the full vertex symbol of the $6^6$ diamondoid net is 6(2).6(2).6(2).6(2).6(2).6(2), the full vertex symbol of the topology in the title compound is 6.6 (2).6.6 (2).6.6 (2).

Non classical C—H···O interactions between phenyl C—H bonds (C6—H6) and longer arm carboxylate O atoms (O3) of the 4-cmb ligands provide some ancillary structural stabilization for the three-dimensional coordination polymer network. The C···O distance across these interactions measures 3.163 (1) Å.

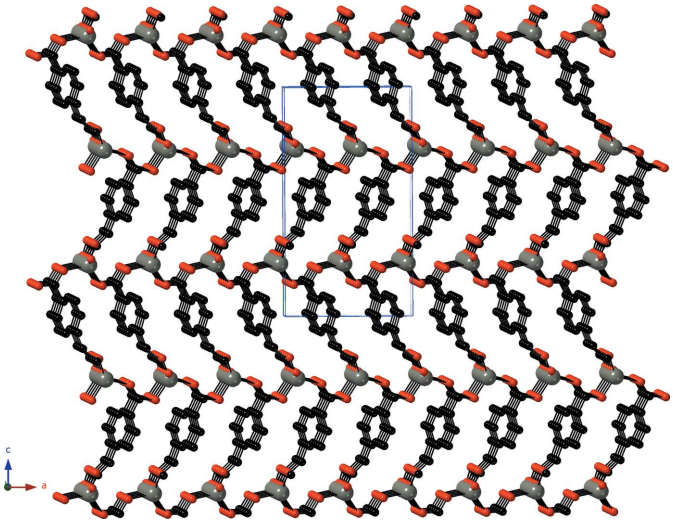


**Figure 3**
A rendering of the three-dimensional $[Zn(4\text{-cmb})]_n$ coordination polymer network in the title compound, viewed down and slightly offset from the *b*-axis direction.

**Table 1**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Zn(C_9H_6O_4)]$ |
| $M_r$ | 243.51 |
| Crystal system, space group | Orthorhombic, $Pca2_1$ |
| Temperature (K) | 173 |
| *a*, *b*, *c* (Å) | 9.6314 (11), 4.8612 (6), 17.269 (2) |
| *V* (Å$^3$) | 808.54 (17) |
| *Z* | 4 |
| Radiation type | Mo *Kα* |
| $\mu$ (mm$^{-1}$) | 3.02 |
| Crystal size (mm) | 0.11 × 0.07 × 0.05 |
| | |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2013) |
| $T_{min}$, $T_{max}$ | 0.608, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 5902, 1474, 1441 |
| $R_{int}$ | 0.026 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.019, 0.049, 1.07 |
| No. of reflections | 1474 |
| No. of parameters | 128 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.41, −0.26 |
| Absolute structure | Refined as an inversion twin |
| Absolute structure parameter | 0.440 (19) |

Computer programs: *COSMO* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

## Synthesis and crystallization

$Zn(NO_3)_2{\cdot}6H_2O$ (110 mg, 0.37 mmol), 4-(carboxymethyl)-benzoic acid (67 mg, 0.37 mmol), bis(4-pyridyl)urea (79 mg,

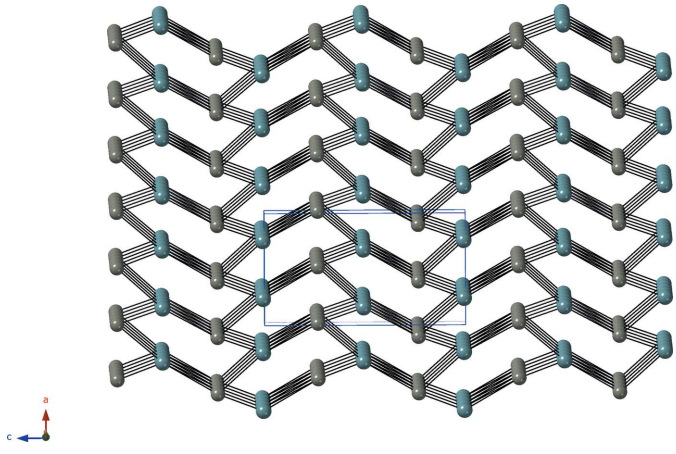


**Figure 4**
A schematic perspective of the 4,4-connected non-diamondoid $6^6$ topology net in the title compound. The Zn atoms are shown in gray, and the centroids of the phenyl rings of the 4-cmb ligands are shown in teal.

0.37 mmol) and 0.75 mL of a 1.0 *M* NaOH solution were placed into 10 mL of distilled $H_2O$ in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 393 K for 2 d, and then cooled slowly to 273 K. Colorless crystals of the title complex (35 mg, 39% yield based on Zn) were isolated after washing with distilled water and acetone, and drying in air.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The crystal of the title compound was an inversion twin, and the structure could not be solved or refined in centrosymmetric space groups.

## Funding information

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## References

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Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

# full crystallographic data

*IUCrData* (2019). **4**, x191014 [https://doi.org/10.1107/S2414314619010149]

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*Crystal data*

$[Zn(C_9H_6O_4)]$
$M_r$ = 243.51
Orthorhombic, $Pca2_1$
$a$ = 9.6314 (11) Å
$b$ = 4.8612 (6) Å
$c$ = 17.269 (2) Å
$V$ = 808.54 (17) Å$^3$
$Z$ = 4
$F(000)$ = 488
$D_x$ = 2.000 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4707 reflections
$\theta$ = 2.4–25.4°
$\mu$ = 3.02 mm$^{-1}$
$T$ = 173 K
Block, colorless
0.11 × 0.07 × 0.05 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.36 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
$T_{min}$ = 0.608, $T_{max}$ = 0.745
5902 measured reflections
1474 independent reflections
1441 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.026
$\theta_{max}$ = 25.4°, $\theta_{min}$ = 2.4°
$h$ = −11→11
$k$ = −5→5
$l$ = −20→20

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.049
$S$ = 1.07
1474 reflections
128 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 0.2338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.41 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.440 (19)

*Special details*

**Experimental**. Data was collected using a BRUKER CCD (charge coupled device) based diffractometer equipped with an Oxford low-temperature apparatus operating at 173 K. A suitable crystal was chosen and mounted on a nylon loop using Paratone oil. Data were measured using omega scans of 0.5° per frame for 30 s. The total number of images were based on results from the program COSMO where redundancy was expected to be 4 and completeness to 0.83Å to 100%. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections.Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS6 multi-scan technique, supplied by George Sheldrick. The structure was solved by the direct method using the SHELXT program and refined by least squares method on F2, SHELXL, incorporated in OLEX2.

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. The structure was refined by Least Squares using version 2018/3 of XL (Sheldrick, 2015) incorporated in Olex2 (Dolomanov *et al.*, 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.56331 (4) | 0.57814 (7) | 0.73682 (2) | 0.01480 (14) |
| O3 | −0.0109 (3) | 0.3545 (6) | 0.32739 (16) | 0.0183 (6) |
| O2 | 0.2616 (3) | 0.4478 (5) | 0.71219 (15) | 0.0190 (7) |
| O4 | −0.0524 (3) | −0.0286 (6) | 0.26387 (17) | 0.0209 (7) |
| O1 | 0.4561 (3) | 0.4858 (7) | 0.64554 (17) | 0.0198 (6) |
| C2 | 0.2647 (4) | 0.3138 (8) | 0.5782 (2) | 0.0171 (8) |
| C5 | 0.1557 (4) | 0.0862 (7) | 0.4423 (2) | 0.0170 (8) |
| C1 | 0.3286 (4) | 0.4242 (7) | 0.6498 (2) | 0.0145 (8) |
| C6 | 0.2485 (4) | 0.3057 (8) | 0.4389 (3) | 0.0191 (8) |
| H6 | 0.2738 | 0.3798 | 0.3900 | 0.023* |
| C8 | 0.1057 (5) | −0.0552 (8) | 0.3698 (3) | 0.0203 (9) |
| H8A | 0.0600 | −0.2290 | 0.3853 | 0.024* |
| H8B | 0.1883 | −0.1051 | 0.3387 | 0.024* |
| C7 | 0.3041 (4) | 0.4171 (7) | 0.5055 (2) | 0.0167 (8) |
| H7 | 0.3691 | 0.5638 | 0.5022 | 0.020* |
| C4 | 0.1169 (4) | −0.0147 (8) | 0.5143 (3) | 0.0190 (8) |
| H4 | 0.0531 | −0.1634 | 0.5173 | 0.023* |
| C9 | 0.0067 (4) | 0.0996 (8) | 0.3177 (2) | 0.0161 (8) |
| C3 | 0.1700 (4) | 0.0985 (7) | 0.5818 (2) | 0.0171 (8) |
| H3 | 0.1415 | 0.0287 | 0.6307 | 0.021* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.0149 (2) | 0.0164 (2) | 0.0131 (2) | −0.00133 (14) | 0.0010 (2) | −0.0021 (2) |
| O3 | 0.0217 (16) | 0.0151 (13) | 0.0181 (14) | 0.0020 (12) | −0.0014 (13) | 0.0002 (11) |
| O2 | 0.0129 (13) | 0.0284 (15) | 0.0156 (15) | 0.0007 (10) | 0.0007 (10) | −0.0013 (11) |
| O4 | 0.0286 (17) | 0.0157 (13) | 0.0185 (15) | 0.0017 (11) | −0.0095 (11) | −0.0052 (11) |
| O1 | 0.0168 (15) | 0.0291 (15) | 0.0136 (15) | −0.0051 (13) | −0.0003 (12) | −0.0045 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.015 (2) | 0.0170 (19) | 0.020 (2) | 0.0027 (15) | 0.0009 (16) | −0.0022 (17) |
| C5 | 0.0162 (19) | 0.0146 (19) | 0.020 (2) | 0.0057 (14) | −0.0049 (18) | −0.0007 (16) |
| C1 | 0.013 (2) | 0.0136 (19) | 0.016 (2) | −0.0007 (14) | −0.0022 (16) | 0.0023 (15) |
| C6 | 0.023 (2) | 0.018 (2) | 0.016 (2) | −0.0001 (18) | 0.0031 (18) | 0.0010 (17) |
| C8 | 0.025 (2) | 0.016 (2) | 0.020 (2) | 0.0022 (16) | −0.0039 (19) | −0.0017 (17) |
| C7 | 0.016 (2) | 0.0153 (19) | 0.019 (2) | −0.0009 (14) | 0.0013 (15) | −0.0004 (16) |
| C4 | 0.016 (2) | 0.0178 (18) | 0.023 (2) | −0.0030 (16) | −0.0008 (17) | −0.0028 (17) |
| C9 | 0.016 (2) | 0.019 (2) | 0.0134 (19) | −0.0016 (15) | 0.0025 (16) | −0.0009 (15) |
| C3 | 0.017 (2) | 0.0184 (19) | 0.016 (2) | −0.0002 (15) | 0.0021 (16) | 0.0020 (16) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—O3$^{i}$ | 1.971 (3) | C2—C3 | 1.390 (6) |
| Zn1—O2$^{ii}$ | 1.961 (3) | C5—C6 | 1.393 (5) |
| Zn1—O4$^{iii}$ | 1.971 (3) | C5—C8 | 1.507 (6) |
| Zn1—O1 | 1.937 (3) | C5—C4 | 1.387 (6) |
| O3—Zn1$^{iv}$ | 1.971 (3) | C6—H6 | 0.9500 |
| O3—C9 | 1.261 (5) | C6—C7 | 1.379 (6) |
| O2—Zn1$^{v}$ | 1.961 (3) | C8—H8A | 0.9900 |
| O2—C1 | 1.262 (5) | C8—H8B | 0.9900 |
| O4—Zn1$^{vi}$ | 1.971 (3) | C8—C9 | 1.511 (6) |
| O4—C9 | 1.256 (5) | C7—H7 | 0.9500 |
| O1—C1 | 1.266 (5) | C4—H4 | 0.9500 |
| C2—C1 | 1.482 (6) | C4—C3 | 1.388 (6) |
| C2—C7 | 1.404 (6) | C3—H3 | 0.9500 |
| | | | |
| O3$^{i}$—Zn1—O4$^{iii}$ | 109.47 (12) | C7—C6—C5 | 121.0 (4) |
| O2$^{ii}$—Zn1—O3$^{i}$ | 112.72 (12) | C7—C6—H6 | 119.5 |
| O2$^{ii}$—Zn1—O4$^{iii}$ | 99.55 (11) | C5—C8—H8A | 107.8 |
| O1—Zn1—O3$^{i}$ | 112.43 (12) | C5—C8—H8B | 107.8 |
| O1—Zn1—O2$^{ii}$ | 109.13 (11) | C5—C8—C9 | 117.9 (3) |
| O1—Zn1—O4$^{iii}$ | 112.90 (14) | H8A—C8—H8B | 107.2 |
| C9—O3—Zn1$^{iv}$ | 118.1 (3) | C9—C8—H8A | 107.8 |
| C1—O2—Zn1$^{v}$ | 132.7 (3) | C9—C8—H8B | 107.8 |
| C9—O4—Zn1$^{vi}$ | 132.9 (3) | C2—C7—H7 | 120.0 |
| C1—O1—Zn1 | 121.7 (3) | C6—C7—C2 | 120.0 (4) |
| C7—C2—C1 | 120.3 (3) | C6—C7—H7 | 120.0 |
| C3—C2—C1 | 120.5 (4) | C5—C4—H4 | 119.5 |
| C3—C2—C7 | 119.2 (4) | C5—C4—C3 | 120.9 (4) |
| C6—C5—C8 | 121.3 (4) | C3—C4—H4 | 119.5 |
| C4—C5—C6 | 118.8 (4) | O3—C9—C8 | 119.7 (4) |
| C4—C5—C8 | 119.8 (3) | O4—C9—O3 | 121.6 (4) |
| O2—C1—O1 | 121.6 (4) | O4—C9—C8 | 118.6 (3) |
| O2—C1—C2 | 122.2 (3) | C2—C3—H3 | 119.9 |
| O1—C1—C2 | 116.1 (4) | C4—C3—C2 | 120.1 (4) |
| C5—C6—H6 | 119.5 | C4—C3—H3 | 119.9 |
| | | | |
| Zn1$^{iv}$—O3—C9—O4 | −25.6 (5) | C1—C2—C3—C4 | −176.1 (4) |

| | | | |
|---|---|---|---|
| Zn1$^{iv}$—O3—C9—C8 | 151.8 (3) | C6—C5—C8—C9 | −71.1 (5) |
| Zn1$^{v}$—O2—C1—O1 | 170.3 (3) | C6—C5—C4—C3 | −0.5 (6) |
| Zn1$^{v}$—O2—C1—C2 | −12.0 (5) | C8—C5—C6—C7 | −173.7 (4) |
| Zn1$^{vi}$—O4—C9—O3 | −173.7 (3) | C8—C5—C4—C3 | 175.0 (4) |
| Zn1$^{vi}$—O4—C9—C8 | 8.9 (6) | C7—C2—C1—O2 | 145.3 (4) |
| Zn1—O1—C1—O2 | 7.6 (5) | C7—C2—C1—O1 | −36.9 (5) |
| Zn1—O1—C1—C2 | −170.3 (3) | C7—C2—C3—C4 | 1.0 (6) |
| C5—C6—C7—C2 | −1.6 (6) | C4—C5—C6—C7 | 1.7 (6) |
| C5—C8—C9—O3 | 13.3 (6) | C4—C5—C8—C9 | 113.6 (4) |
| C5—C8—C9—O4 | −169.2 (4) | C3—C2—C1—O2 | −37.7 (5) |
| C5—C4—C3—C2 | −0.8 (6) | C3—C2—C1—O1 | 140.2 (4) |
| C1—C2—C7—C6 | 177.3 (4) | C3—C2—C7—C6 | 0.2 (6) |

Symmetry codes: (i) −*x*+1/2, *y*, *z*+1/2; (ii) *x*+1/2, −*y*+1, *z*; (iii) −*x*+1/2, *y*+1, *z*+1/2; (iv) −*x*+1/2, *y*, *z*−1/2; (v) *x*−1/2, −*y*+1, *z*; (vi) −*x*+1/2, *y*−1, *z*−1/2.