

## Poly[( $\mu_2$ -1,3-di-4-pyridylpropane- $\kappa^2$ N:N')( $\mu_3$ -glutarato- $\kappa^3$ O:O':O'')-dizinc(II)]

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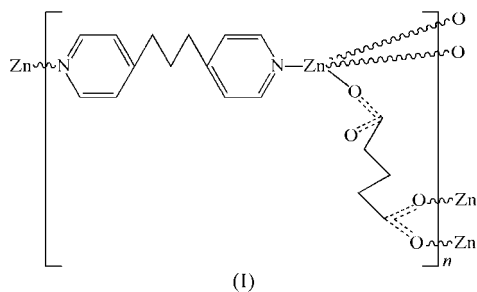
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The title compound,  $[\text{Zn}_2(\text{C}_5\text{H}_6\text{O}_4)_2(\text{C}_{13}\text{H}_{14}\text{N}_2)]_n$  or  $[\text{Zn}_2(\text{glu})_2(\text{bpp})]_n$ , is a novel zinc polymer based on mixed flexible glutarate (glu) and 1,3-di-4-pyridylpropane (bpp) ligands. The  $\text{Zn}^{\text{II}}$  center has a distorted tetrahedral geometry and the central atom of the bpp ligand is located at a special site with a  $C_2$  axis passing through it. A layer is formed by Zn–glu bonding. Such layers are pillared by bpp ligands, forming a three-dimensional framework with large channels. The inverted interpenetration of two three-dimensional frameworks completes the molecular structure.

### Comment

The use of versatile multidentate ligands to design metal-organic coordination polymers has mushroomed recently, not only because such ligands can form intriguing structural topologies (Yaghi *et al.*, 1998; Hagrman *et al.*, 1999), but also because they have unexpected properties with potential applications as functional materials (Piguet *et al.*, 1997; Park *et al.*, 2001). Some organic N-atom donors, such as bipyridines



and their analogues, are often chosen to modify the structures and properties of these polymers (Davidson & Loeb, 2003; Biradha *et al.*, 1999). In addition, long flexible multidentate ligands have shown the ability to produce unique interwoven extended structural motifs, such as polycatenanes (Carlucci *et al.*, 2003), polyrotaxanes (Poleschak *et al.*, 2004; Wang *et al.*,

2004), double helices (Piguet *et al.*, 1997) and other uncommon species (Carlucci, Ciani & Proserpio, 2004; Carlucci, Ciani, Proserpio & Spadacini, 2004). The 1,3-di-4-pyridylpropane (bpp) ligand, as an analogue of 4,4'-bipyridine, possesses variable flexibility and functionality owing to the introduction of three methylene groups between the two pyridyl rings (Mukherjee *et al.*, 2003; Wen *et al.*, 2005). The saturated aliphatic dicarboxylate ligands, which exhibit conformational and coordination versatility due to the presence of single-bonded carbon chains, are also an attractive choice and are viewed as important flexible spacer ligands. As an elementary member of the  $\alpha,\omega$ -dicarboxylate family, the glutarate anion has proven to be a versatile polydentate ligand (Zheng *et al.*, 2004). However, metal coordination polymers based on mixed bpp and glutarate (glu) ligands, to our knowledge, have not been reported to date. In this paper, we

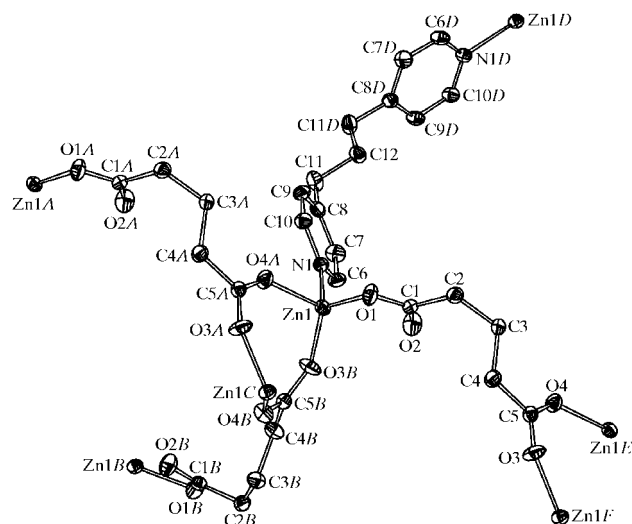


Figure 1

A view of (I), shown with 30% probability displacement ellipsoids; H atoms have been omitted. [Symmetry codes: (A)  $\frac{1}{2} + x, -\frac{1}{2} + y, z$ ; (B)  $-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$ ; (C)  $-x, y, -\frac{1}{2} - z$ ; (D)  $-x, y, \frac{1}{2} - z$ ; (E)  $-\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (F)  $-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$ .]

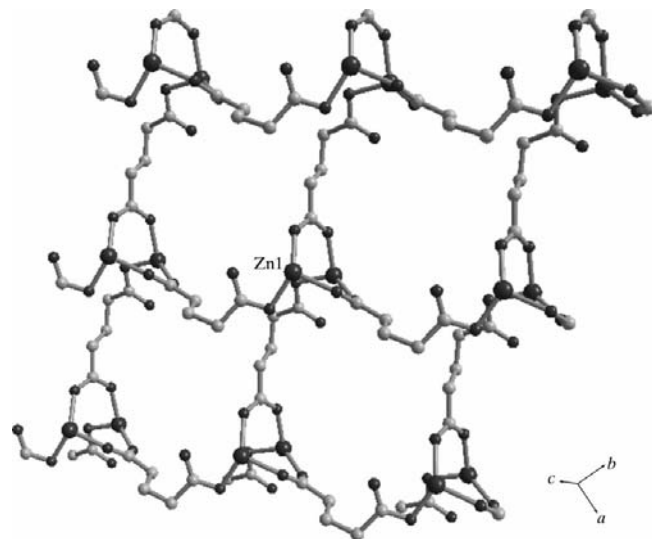


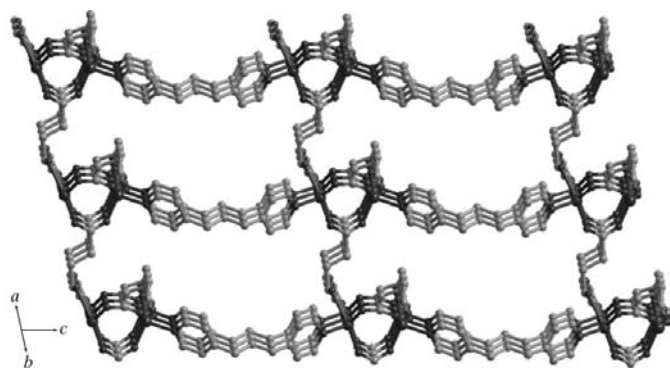
Figure 2

The layered structure in (I), showing Zn atoms bridged by glu ligands.

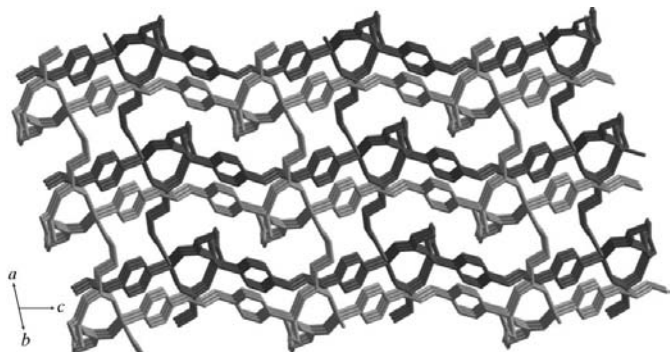
report a novel Zn polymer,  $[\text{Zn}_2(\text{glu})_2(\text{bpp})]_n$ , (I), which features a three-dimensional architecture with interpenetration.

As shown in Fig. 1, the  $\text{Zn}^{\text{II}}$  center has a distorted tetrahedral geometry, which is defined by one of the pyridyl N atoms of the bpp ligand and three O atoms from three carboxylate groups of three different glu ligands (Table 1). The two carboxylate groups of the glu ligand have different coordination modes; one bridges two Zn atoms in a bidentate *syn-syn* fashion, the shortest  $\text{Zn}\cdots\text{Zn}$  distance being 3.569 (1) Å, while the other carboxylate group coordinates to the Zn atom in a monodentate fashion. The shortest  $\text{Zn}\cdots\text{Zn}$  distance between Zn atoms separated by a glu ligand is 8.786 (1) Å. The angle between the planes of the two carboxylate groups is 77.02°. The twist in the glu ligand occurs at atom C3; the C1–C2–C3–C4 torsion angle is 71.2 (6)°. The bpp ligand acts as a  $\mu_2$ -bridge and links two symmetry-related Zn centers, with a  $\text{Zn}\cdots\text{Zn}$  separation of 13.567 (2) Å. Atom C12 is located on a special site with a  $C_2$  axis passing through it. The twist in the bpp ligand also occurs at atom C12; the C8–C11–C12–C11(–x, y,  $\frac{1}{2}$  – z) torsion angle is 174.5 (6)°. The angle between the two pyridyl planes of the bpp ligand is 60.7°.

As shown in Fig. 2, the Zn atoms are interlinked by the glu ligands to generate a layer parallel to (111). The resulting layer is composed of 8- and 36-membered rings. It is inter-



**Figure 3**  
Topology of the structure of complex (I), showing layers being pillared by the flexible bpp ligands and the formation of large channels.



**Figure 4**  
The inverted interpenetration framework of (I).

esting to note that no inversion center can be found in this layer. Such a layer can also be looked at as the vertical assembly of two groups of parallel chains with the dimetal units functioning as hinges. As shown in Fig. 3, the resulting layers are pillared by the flexible bpp ligands to form a three-dimensional open framework, which contains large channels along the *b* axis of dimensions 17.135 (2) × 8.786 (2) Å. Large channels can also be found along the *a* or *c* axes. Owing to the orderly connection of the asymmetrical layers, there is no inversion center in a single open framework. However, the void spaces in the single framework are so large that two three-dimensional frameworks can interpenetrate each other, so as to complete the final three-dimensional architecture (Fig. 4). An inversion center exists between the two independent frameworks owing to their inverted interpenetration.

In summary, we have successfully synthesized and structurally characterized a novel Zn polymer based on mixed flexible glu and bpp ligands. It is the first example of a coordination polymer composed of two such long flexible ligands.

### Experimental

A mixture of  $\text{ZnCl}_2$  (0.13 g, 1.0 mmol) with glutaric acid (0.13 g, 1.0 mmol), bpp (0.10 g, 0.5 mmol) and NaOH (0.04 g, 1 mmol), in the molar ratio 2:2:1:2, and water (20 ml) was placed in a Parr Teflon-lined stainless steel vessel (25 ml); the vessel was sealed and heated to 433 K for 3 d, and the reaction mixture was cooled at a rate of 0.3 K  $\text{min}^{-1}$ , leading to the formation of colorless (I) in a yield of 53% based on bpp. Analysis calculated for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_8\text{Zn}_2$ : C 46.88, H 4.45, N 4.75%; found: C 47.00, H 4.76, N 4.64%. IR (solid KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 1611 (vs), 1570 (s), 1383 (s), 1294 (w), 1215 (m), 1085 (w), 1017 (w), 817 (m), 635 (m), 495 (w).

#### Crystal data

$[\text{Zn}_2(\text{C}_5\text{H}_6\text{O}_4)_2(\text{C}_{13}\text{H}_{14}\text{N}_2)]$	$Z = 4$
$M_r = 589.24$	$D_x = 1.607 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 10.5886$ (15) Å	$\mu = 2.02 \text{ mm}^{-1}$
$b = 14.0238$ (19) Å	$T = 293$ (2) K
$c = 17.135$ (2) Å	Prism, colorless
$\beta = 106.838$ (2)°	$0.15 \times 0.10 \times 0.08 \text{ mm}$
$V = 2435.3$ (6) Å <sup>3</sup>	

#### Data collection

Bruker SMART CCD area-detector diffractometer	3817 measured reflections
$\varphi$ and $\omega$ scans	2158 independent reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)	1619 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.785$ , $T_{\text{max}} = 0.851$	$R_{\text{int}} = 0.032$
	$\theta_{\text{max}} = 25.1^\circ$

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 8.7107P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
2158 reflections	$\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$
159 parameters	
H-atom parameters constrained	

H atoms bonded to C atoms were positioned geometrically and refined using a riding model [aromatic C–H = 0.93 Å, aliphatic C–H = 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

**Table 1**

Selected geometric parameters (Å, °).

Zn1—O1	1.935 (4)	Zn1—O4 <sup>ii</sup>	1.991 (3)
Zn1—O3 <sup>i</sup>	1.940 (3)	Zn1—N1	2.039 (4)
O1—Zn1—O3 <sup>i</sup>	128.16 (17)	O3 <sup>i</sup> —Zn1—N1	97.82 (16)
O1—Zn1—O4 <sup>ii</sup>	99.88 (14)	O4 <sup>ii</sup> —Zn1—N1	95.28 (15)
O1—Zn1—N1	118.37 (17)		

Symmetry codes: (i)  $-x - \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ .

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3006). Services for accessing these data are described at the back of the journal.

**References**

- Biradha, K., Seward, C. & Zaworotko, M. J. (1999). *Angew. Chem. Int. Ed.* **38**, 492–495.
- Bruker (2002). *SMART, SAINT and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Carlucci, L., Ciani, G. & Proserpio, D. M. (2003). *CrystEngComm*, **5**, 269–279.
- Carlucci, L., Ciani, G. & Proserpio, D. M. (2004). *Chem. Commun.* pp. 380–381.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Spadacini, L. (2004). *CrystEngComm*, **6**, 96–101.
- Davidson, G. J. E. & Loeb, S. J. (2003). *Angew. Chem. Int. Ed.* **42**, 74–77.
- Hagman, P. J., Hagman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.
- Mukherjee, P. S., Konar, S., Zangrando, E., Mallah, T., Ribas, J. & Chaudhuri, N. R. (2003). *Inorg. Chem.* **42**, 2695–2703.
- Park, H. W., Sung, S. M., Min, K. S., Bang, H. & Suh, M. P. (2001). *Eur. J. Inorg. Chem.* pp. 2865–2869.
- Piguet, C., Bernardinelli, G. & Hopfgartner, G. (1997). *Chem. Rev.* **97**, 2005–2062.
- Poleschak, I., Kern, J. M. & Sauvage, J. P. (2004). *Chem. Commun.* pp. 474–476.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Wang, Q. C., Qu, D. H., Ren, J., Chen, K. C. & Tian, H. (2004). *Angew. Chem. Int. Ed.* **43**, 2661–2665.
- Wen, Y. H., Zhang, J., Wang, X. Q., Feng, Y. L., Cheng, J. K., Li, Z. J. & Yao, Y. G. (2005). *New J. Chem.* **29**, 995–997.
- Yaghi, O. M., Li, H., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.
- Zheng, Y. Q., Lin, J. L. & Kong, Z. P. (2004). *Inorg. Chem.* **43**, 2590–2596.