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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.025
 wR factor = 0.071
Data-to-parameter ratio = 13.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis[*N*-(2-pyridylmethyl)glycinato]zinc(II) dihydrate

In the mononuclear title complex, $[\text{Zn}(\text{PMG})_2]\cdot 2\text{H}_2\text{O}$ or $[\text{Zn}(\text{C}_8\text{H}_9\text{N}_2\text{O}_2)_2]\cdot 2\text{H}_2\text{O}$, the Zn^{II} center is surrounded by two *N*-(2-pyridylmethyl)glycinate (PMG) ligands, which impose a distorted octahedral environment on the metal. Two deprotonated molecules of the new tridentate *N,N',O*-donor ligand HPMG are facially coordinated to the Zn^{II} center in such a way that the atoms of the same kind are mutually *trans* to each other, generating a centrosymmetric structure.

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Comment

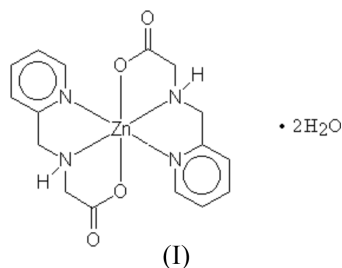
Zinc complexes are of great interest in organic synthesis and in bioinorganic chemistry. In the former, zinc complexes are used in stereospecific organic reactions (Lebel *et al.*, 2003; Abufarag & Vahrenkamp, 1995a). In bioinorganic chemistry, it is well known that zinc plays an important role in many biological processes (Kimura, 1994; Vallee & Auld, 1993; Uhlenbrock *et al.*, 1996), so that Zn^{II} coordinated by a strategic ligand can lead to a structural and/or functional model for zinc metalloenzymes.

Modeling the metal binding site of zinc metalloenzymes is a goal that has been pursued by bioinorganic chemists over the past few years. Studies on the coordination chemistry of Zn^{II} with carboxylate ligands have aroused a growing interest during the last decade in view of the biological modeling applications (Chen & Tong, 1994; Sun *et al.*, 2001; Vaira *et al.*, 1998; Abufarag & Vahrenkamp, 1995b). Several zinc model complexes have been developed (Barbarin *et al.*, 1994; Vaira *et al.*, 1998; Abufarag & Vahrenkamp, 1995a). However, one of the difficulties of the model approach is the synthesis of complexes with biologically relevant ligands. Thus, synthetic strategies employing pyridine and carboxylate groups to design new ligands have been focused on mimicking the histidine and aspartate amino acids, which are present in a large number of metalloenzymes (Chen & Tong, 1994; Neves *et al.*, 1997; Riesen *et al.*, 1991).

Some carboxylate derivatives, which have two N atoms of pyridine or amine moieties and one O atom of a carboxylate group, have been previously reported, *e.g.* *N,N*-bis(2-picolyl)- β -alanine (Hazell *et al.*, 1993), *N,N*-bis(2-aminoethyl)glycine (Mao *et al.*, 1992) and *N,N*-bis(2-picolyl)glycine (BPG; Cox *et al.*, 1988). In attempts to model zinc enzymes, the octahedral complex $[\text{Zn}(\text{BPG})(\text{H}_2\text{O})_2]\text{NO}_3\cdot\text{H}_2\text{O}$ may be considered a structural model for the reactive center of the glyoxalase I enzyme, which, according to spectroscopic data, contains a hexacoordinate zinc ion bonded to an *N,O*-donor set (Abufarag & Vahrenkamp, 1995b).

In this report, we present the synthesis of the new ligand *N*-(2-pyridylmethyl)glycine (HPMG) and the first crystal structure of its Zn^{II} mononuclear complex,

$[\text{Zn}(\text{PMG})_2] \cdot 2\text{H}_2\text{O}$, (I), as a further interesting model for mononuclear zinc-containing enzymes.



The molecular structure of the title complex consists of a neutral $\text{Zn}(\text{PMG})_2$ unit and two water molecules of crystallization. In the crystal structure of (I), the Zn atom is located on a special position, lying at a center of symmetry, so that the two PMG^- ligands in the coordination sphere of the metal ion are related by symmetry. The deprotonated PMG^- ligands are facially coordinated to the Zn^{II} ion through the two N- (amine and pyridine) and one O-atom (carboxylate) donors (Fig. 1). Since the molecule of $\text{Zn}(\text{PMG})_2$ is centrosymmetric, atoms of the same kind (two N_{amine} , two $\text{N}_{\text{pyridine}}$ and two $\text{O}_{\text{carboxylate}}$) are coordinated in *trans* positions with respect to each other. The *cis* angles $\text{O1}-\text{Zn1}-\text{N2}$ [$81.99(6)^\circ$] and $\text{N2}-\text{Zn1}-\text{N1}$ [$78.54(7)^\circ$] are significantly smaller than the ideal octahedral angle of 90° (Table 1). These angles reflect the restriction imposed by formation of the five-membered chelate rings and also reflect the distortion in the octahedral environment around the metal center.

The bond length $\text{Zn}-\text{N}_{\text{pyridine}}$ [2.1864 (17) Å] is the longest in the coordination sphere in $\text{Zn}(\text{PMG})_2$ and is similar to those observed in other octahedral zinc complexes: $[\text{Zn}^{\text{II}}(\text{BPA})_2] \cdot 2\text{H}_2\text{O}$, average 2.163 Å (Neves *et al.*, 1997), where BPA is bis[(2-hydroxybenzyl)(2-methylpyridyl)amine]; $[\text{Zn}(\text{BPG})(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$, average 2.120 Å (Abufarag & Vahrenkamp, 1995b); $\text{Zn}(\text{TETAH}_2) \cdot 4\text{H}_2\text{O}$, average 2.181 Å (Riesen *et al.*, 1991), where TETAH_4 is 1,4,8,11-tetraazacyclotetradecane-*N,N',N'',N'''*-tetraacetic acid; $[\text{ZnL}]\text{ClO}_4 \cdot \text{H}_2\text{O}$, average 2.077 Å (Vaira *et al.*, 1998), where *L* is 1,4-bis-(1-methylimidazol-2-ylmethyl)-7-carboxymethyl-1,4,7-triazacyclononane); and $[\text{Zn}(\text{bipyridine})_3](\text{ClO}_4)_2$, average 2.157 Å (Chen *et al.*, 1995), in which the Zn^{II} is attached to the pyridine groups. The $\text{Zn}-\text{N}_{\text{amine}}$ distance of 2.1210 (17) Å in the title compound is somewhat shorter but also comparable to the corresponding bonds in the following hexacoordinated Zn^{II} complexes: $[\text{Zn}(\text{BPA})_2] \cdot 2\text{H}_2\text{O}$, $\text{Zn1}-\text{N}_{\text{amine}} = 2.148(8)$ Å and $\text{Zn2}-\text{N}_{\text{amine}} = 2.186(7)$ Å (Neves *et al.*, 1997); and $[\text{Zn}(\text{BPG})(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$, average 2.198 Å (Abufarag & Vahrenkamp, 1995b). The unique $\text{Zn}-\text{O}_{\text{carboxylate}}$ bond length in $\text{Zn}(\text{PMG})_2$ is 2.0964 (15) Å, which is shorter than those generally found in other octahedral complexes, such as 2.135 (2) Å (Abufarag & Vahrenkamp, 1995b) and 2.127 Å (Riesen *et al.*, 1991).

An extensive hydrogen-bond network is observed in the three-dimensional packing of (I). The water molecules and

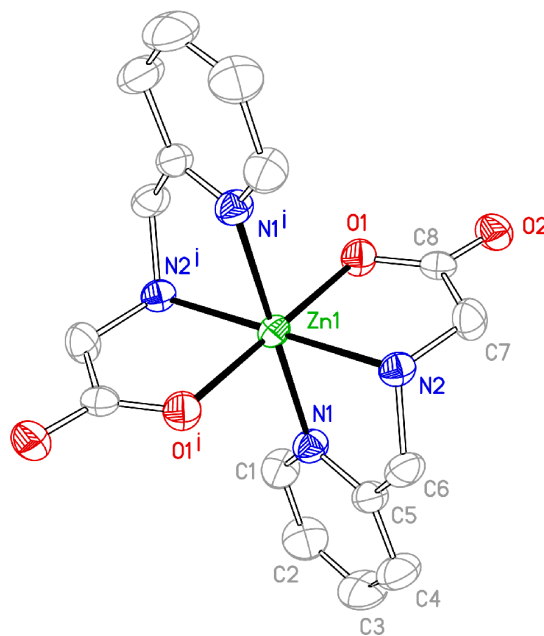


Figure 1

A view of the structure of (I) with the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted. [Symmetry code: (i) $1 - x, -y, -z$.]

amine groups are hydrogen bonded to neighboring molecules, forming infinite two-dimensional aggregations that are parallel to the (100) plane. In this intricate arrangement the protonated groups (water and amine) only act as proton donors, while the O atoms from carboxylate moieties are the proton acceptors. Geometric parameters of the hydrogen-bond network are listed in Table 2.

In summary, we have synthesized and structurally characterized a new mononuclear Zn^{II} complex containing *N,O*-donor groups which are able to mimic bonded histidine and aspartate/glutamate amino acids in zinc metalloenzymes.

Experimental

The HPMG ligand was prepared in high yield by a condensation reaction between a methanolic solution of glycine (1.27 g, 17 mmol), previously neutralized with LiOH (1.42 g, 17 mmol), and 2-pyridinecarboxaldehyde (1.82 g, 17 mmol). The reaction mixture was stirred for 2 h at 273 K. The solvent was evaporated and water (50 ml) was added. The pH was adjusted to 7.0 with 1 M HCl, and the aqueous phase was extracted with three 50 ml portions of CH_2Cl_2 , and the extracts were combined, dried over anhydrous MgSO_4 , filtered off and evaporated. The oily residue was dissolved in methanol and then reduced by catalytic hydrogenation (Pd/C 5%) for 24 h. The catalyst was filtered off and the resulting solution was evaporated under reduced pressure, yielding a clear oil that was used without further purification (yield 2.82 g, 100%). Spectroscopic analysis: ^1H NMR ($\text{CDCl}_3 + \text{D}_2\text{O}$, δ , p.p.m): 3.46 (s, 2H, CH_2), 3.94 (s, 2H, CH_2), 7.14–7.69 (m, 3H, CH_{arom}), 8.55 (s, 1H, CH_{arom}). The zinc complex was obtained by addition of one equivalent of $[\text{Zn}(\text{CH}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$ to a methanolic solution containing two equivalents of HPMG, affording a colorless solution. Crystals of $[\text{Zn}(\text{PMG})_2] \cdot 2\text{H}_2\text{O}$ suitable for X-ray analysis were obtained by slow evaporation of the solvent.

Crystal data

Zn(C₈H₉N₂O₂)₂·2H₂O
M_r = 431.75
 Monoclinic, *P*2₁/*c*
a = 9.081 (2) Å
b = 9.480 (2) Å
c = 10.834 (2) Å
 β = 91.99 (3)°
V = 932.1 (3) Å³
Z = 2
D_x = 1.538 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 8.3–18.2°
 μ = 1.36 mm⁻¹
T = 293 (2) K
 Irregular block, colorless
 0.30 × 0.23 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (PLATON; Spek, 1990)
T_{min} = 0.702, *T_{max}* = 0.794
 1930 measured reflections
 1827 independent reflections
 1448 reflections with *I* > 2 σ (*I*)
R_{int} = 0.015
 θ_{\max} = 26.0°
h = -11 → 11
k = -11 → 0
l = -13 → 0
 3 standard reflections every 200 reflections
 intensity decay: 1%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.025
wR(*F*²) = 0.071
S = 1.03
 1827 reflections
 137 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.3276P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0109 (13)

Table 1
 Selected geometric parameters (Å, °).

Zn1—O1	2.0964 (15)	Zn1—N1	2.1864 (17)
Zn1—N2	2.1210 (17)		
O1—Zn1—N2 ⁱ	98.01 (6)	N2—Zn1—N1 ⁱ	101.46 (7)
O1—Zn1—N2	81.99 (6)	O1—Zn1—N1	90.33 (7)
O1—Zn1—N1 ⁱ	89.67 (7)	N2—Zn1—N1	78.54 (7)

Symmetry code: (i) 1 - *x*, -*y*, -*z*.

Table 2
 Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2N...O2 ⁱⁱ	0.83 (2)	2.20 (2)	2.998 (2)	162 (2)
O1W—H1W...O2 ⁱⁱⁱ	0.78 (3)	2.07 (3)	2.820 (3)	163 (3)
O1W—H2W...O1 ^{iv}	0.86 (4)	2.02 (4)	2.876 (3)	174 (3)

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

H atoms bonded to C atoms were placed in calculated positions, with C—H distances ranging from 0.93 to 0.97 Å, and included in the refinement in riding-motion approximation with *U_{iso}* = 1.2*U_{eq}* of the carrier atom. H atoms bonded to N and O atoms were refined independently with isotropic displacement parameters

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: SET4 in CAD-4 EXPRESS; data reduction: HELENA (Spek, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ZORTEP (Zsolnai et al., 1996); software used to prepare material for publication: SHELXL97.

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