

Tris[(*R*)-lactamide- κ^2O,O']zinc(II) tetrabromozincate

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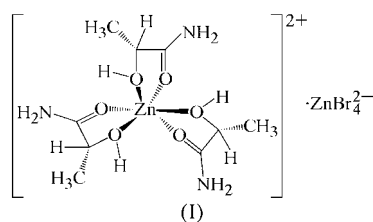
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The title compound, tris[(*R*)-2-hydroxypropanamide- κ^2O,O']zinc(II) tetrabromozincate, $[\text{Zn}(\text{C}_3\text{H}_7\text{NO}_2)_3][\text{ZnBr}_4]$, contains one monomeric six-coordinate zinc complex cation and one tetrahedral $[\text{ZnBr}_4]^{2-}$ anion. Both Zn^{II} atoms lie on threefold axes. Coordination in the cation occurs *via* the amide and hydroxy O atoms [$\text{Zn}-\text{O} = 2.074$ (5) and 2.073 (6) Å] and has a distorted octahedral geometry, with *cis*-O–Zn–O angles in the range 76.2 (2)– 109.2 (2)°. In the crystal structure, the cations and anions are linked by $\text{N}-\text{H}\cdots\text{Br}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, generating a three-dimensional network.

Comment

Metal-containing proteins have been studied in relation to severe diseases. Alzheimer's and mad cow diseases imply metal–protein interactions, and metalloproteases are implied in cancer dispersion and angiotensin converting enzyme (ACE) in blood pressure control. For these reasons, amide–metal complexes have attracted much interest. Following our work on metal–amide crystalline complexes (Bekaert *et al.*, 2002*a,b*, 2003), we now report a new zinc complex, (I), with 2-hydroxypropanamide (lactamide).



Compound (I) (Fig. 1) contains one monomeric six-coordinate zinc complex cation, $[\text{Zn}(\text{C}_3\text{H}_7\text{NO}_2)_3]^{2+}$, and one tetrahedral $[\text{ZnBr}_4]^{2-}$ anion. In both the cation and the anion, the Zn atoms lie on threefold axes in space group $P6_3$. In the

cation, the Zn atom is surrounded by three symmetry-related (*R*)-lactamide ligands, coordinated in a bidentate fashion *via* amide atom O1 and hydroxy atom O2, and their symmetry equivalents. The Zn coordination may be described as distorted octahedral. The $\text{O1}-\text{Zn1}-\text{O1}^*$ angles [* is either at $(1-x+y, 2-x, z)$ or $(2-y, 1+x-y, z)$] are 91.6 (2)°,

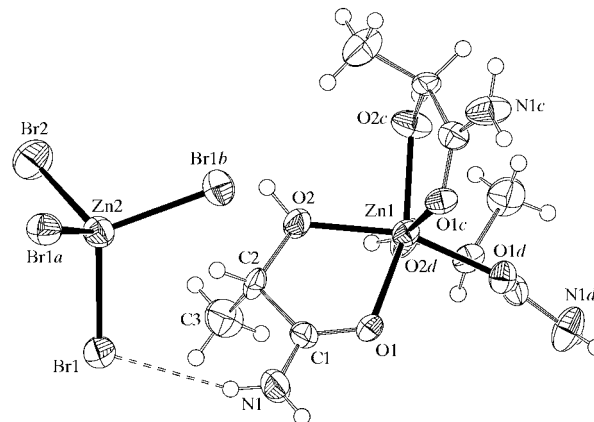


Figure 1
A view of the title compound showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. The suffixes *a*, *b*, *c* and *d* denote atoms at equivalent positions $(1-y, 1+x-y, z)$, $(-x+y, 1-x, z)$, $(2-y, 1+x-y, z)$ and $(1-x+y, 2-x, z)$, respectively.

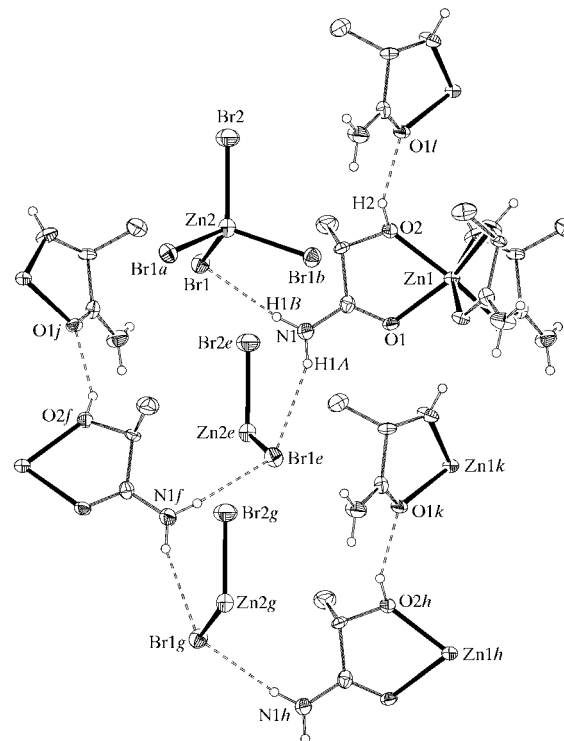


Figure 2
A view showing part of the $\text{N}-\text{H}\cdots\text{Br}$ and $\text{O}-\text{H}\cdots\text{Br}$ hydrogen-bond network in the title compound. Displacement ellipsoids are shown at the 30% probability level for non-H atoms. The atoms in the $\text{Zn2}-\text{Br2}$ bond lie along the *z* direction, with coordinates $(\frac{1}{3}, \frac{2}{3}, z)$. The suffixes denote atoms at the following equivalent positions: *a* $(1-y, 1+x-y, z)$, *b* $(-x+y, 1-x, z)$, *e* = *f* $(1-x, 2-y, -\frac{1}{2}+z)$, *g* = *h* $(x, y, -1+z)$, *k* $(1+x-y, x, -\frac{1}{2}+z)$ and *l* $(1+x-y, x, \frac{1}{2}+z)$.

while the O2—Zn1—O2* angles are 88.1 (2)°. The Zn1(O1)₃ and Zn1(O2)₃ moieties are rotated about the threefold axis, some 31° from a fully eclipsed conformation, and the three symmetry-related *trans*-O—Zn—O angles are 156.0 (2)°. The two Zn—O distances (Table 1) are not significantly different and are in agreement with those reported in the literature. Among the rare crystal structures of metal complexes with lactamide or its derivatives, described in the literature, two coordination modes are possible, *viz.* *N,O*-coordination in chloro[*N*-(pyridin-2-ylmethyl)lactamidato]copper(II) hydrate (Tounsi *et al.*, 2004) and *O,O*-coordination for the lactamide moiety in a molybdenum(VI)-oxodiperoxo complex containing *N,N*-dimethyl lactamide (Winter *et al.*, 1980); the latter structure is similar to that of (I), with the same geometry for the lactamide entity.

In the crystal structure, the individual cation complexes are linked into chains running parallel to the *c* axis by inter-ion N—H···O hydrogen bonds (Table 2 and Fig. 2). Such chains are crosslinked *via* the O2 hydroxy group, forming inter-cation O—H···O hydrogen bonds with amide atom O1. The fact that both atom Zn1 and atom Zn2 lie on threefold axes in space group *P*6₃ then leads to a three-dimensional hydrogen-bonded network.

Experimental

Compound (I) was prepared by mixing a solution of (*R*)-lactamide (0.272 g, 3 mmol) in hot acetic acid (5 ml, 353 K) and a solution of ZnBr₂ (0.496 g, 2 mmol) in boiling acetic acid (10 ml). Upon slow cooling, crystals of (I) were recovered.

Crystal data

[Zn(C ₃ H ₇ NO ₂) ₃][ZnBr ₄]	<i>D_m</i> measured by flotation in CCl ₄ /C ₂ H ₄ Br ₂
<i>M_r</i> = 717.67	Mo <i>K</i> α radiation
Hexagonal, <i>P</i> 6 ₃	Cell parameters from 25 reflections
<i>a</i> = 11.337 (5) Å	<i>θ</i> = 7.5–13.6°
<i>c</i> = 9.910 (5) Å	<i>μ</i> = 9.45 mm ⁻¹
<i>V</i> = 1103.1 (9) Å ³	<i>T</i> = 293 K
<i>Z</i> = 2	Parallelepiped, colourless
<i>D_x</i> = 2.161 Mg m ⁻³	0.30 × 0.20 × 0.15 mm
<i>D_m</i> = 2.14 (2) Mg m ⁻³	

Data collection

Enraf–Nonius CAD-4 diffractometer	818 reflections with <i>I</i> > 2σ(<i>I</i>)
ω–2θ scans	<i>R_{int}</i> = 0.130
Absorption correction: empirical multi-scan (SADABS; Sheldrick, 1996; Blessing, 1995)	<i>θ_{max}</i> = 30.0°
<i>T_{min}</i> = 0.131, <i>T_{max}</i> = 0.284	<i>h</i> = –15 → 15
6629 measured reflections	<i>k</i> = –15 → 15
1109 independent reflections	<i>l</i> = 0 → 13
	3 standard reflections
	frequency: 60 min
	intensity decay: 1%

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.1638P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.02	Δρ _{max} = 0.66 e Å ⁻³
1109 reflections	Δρ _{min} = –0.70 e Å ⁻³
75 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.06 (6)

C- and N-bound H atoms were placed in calculated positions, with C—H distances of 0.96 or 0.98 Å, N—H distances of 0.86 Å and

Table 1

Selected geometric parameters (Å, °).

Zn1—O2	2.073 (6)	Br1—Zn2	2.4315 (15)
Zn1—O1	2.074 (5)	Br2—Zn2	2.377 (3)
N1—C1	1.312 (10)		
O2—Zn1—O2 ⁱ	88.1 (2)	C2—O2—Zn1	118.7 (4)
O2 ⁱ —Zn1—O1	156.0 (2)	Br2—Zn2—Br1	109.15 (6)
O1—Zn1—O1 ⁱⁱ	91.6 (2)	Br1—Zn2—Br1 ⁱⁱⁱ	109.79 (6)
C1—O1—Zn1	117.1 (5)		

Symmetry codes: (i) 2 – *y*, 1 + *x* – *y*, *z*; (ii) 1 – *x* + *y*, 2 – *x*, *z*; (iii) 1 – *y*, 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>
O2—H2···O1 ^{iv}	0.90	1.82	2.696 (8)	166
N1—H1A···Br1 ^v	0.86	2.68	3.487 (8)	157
N1—H1B···Br1	0.86	2.66	3.478 (8)	158

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

*U*_{iso}(H) values of 1.2*U*_{eq}(C,N), and were refined in the riding-model approximation. Coordinates for hydroxy atom H2 were located in a difference map and were then allowed for as riding, with a *U*_{iso}(H) value of 1.2*U*_{eq}(O). The absolute configuration of (I) was known from the synthesis route and the Flack (1983) parameter is entirely in agreement with the known configuration.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1801). Services for accessing these data are described at the back of the journal.

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