Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

catena-Poly[[dibromozinc(**II**)]-*μ*-(*R*,*R*)-1,2-diacetamidocyclohexane]

Alain Bekaert,[a] Pascale Lemoine,[b]* Jean Daniel Brion[a] and Bernard Viossat[c]

[a]Université de Paris XI, Faculté des Sciences Pharmaceutiques et Biologiques, Laboratoire de Chimie Thérapeutique BioCIS, UPRES-A 8076 CNRS, 5 rue J. B. Clément, 92296 Châtenay-Malabry Cedex, France, [b]Université de Paris V, Faculté des Sciences Pharmaceutiques et Biologiques, Laboratoire de Cristallographie et RMN Biologiques, UMR 8015 CNRS, 4 avenue de l'Observatoire, 75270 Paris Cedex 06, France, and [c]Université de Paris V, Faculté des Sciences Pharmaceutiques et Biologiques, Laboratoire de Cristallographie et RMN Biologiques, UMR 8015 CNRS, 4 avenue de l'Observatoire, 75270 Paris Cedex 06, France, and Laboratoire de Chimie Générale, Faculté de Médecine et de Pharmacie, 34 rue du Jardin des Plantes, BP199 86005 Poitiers Cedex, France

Correspondence e-mail:
lemoine@pharmacie.univ-paris5.fr

Received 18 June 2003
Accepted 30 June 2003
Online 10 July 2003

The asymmetric unit of the title compound, [$ZnBr_2(C_{10}H_{18}N_2O_2)$], contains a fragment of the polymeric chain [(*R*,*R*)-1,2-diacetamidocyclohexanedibromozinc(II)]$_n$. The Zn atom is coordinated by two bromide anions and two 1,2-diacetamidocyclohexane (DCH) ligands acting as 1,8-bridging *via* the O atoms. The complex exhibits a distorted tetrahedral geometry around the Zn atom. The crystal packing is characterized by several van der Waals contacts, these interactions resulting in chains parallel to the *b* axis.

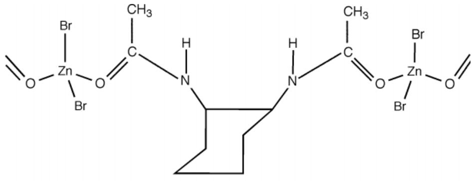
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.010 Å
R factor = 0.031
wR factor = 0.076
Data-to-parameter ratio = 15.1

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

Comment

Zinc is an important metal in chemistry and biochemistry. Zn metalloproteases are of special interest due to their biological activity. Binding of metal ions to amides is of special relevance to conformation transitions of polypeptides. Whereas the solvated structure of Zn^{II} in *N*,*N*-dimethylformamide was previously studied (Ozutsumi *et al.*, 1993; Suzuki *et al.*, 1991), the study of Zn^{II} complexes with chiral amidic ligands would be of current interest due to their potential use as models for Zn-containing enzymes. Our experience of crystalline organometallic complexes such as $Al(DMF)_6(Br_3)_3$ (Bekaert *et al.*, 2002*a*) and $B(DMA)_4(Br_3)_2Br$ (Bekaert *et al.*, 2002*b*), based on metal–amide bonds, led us to investigate a crystalline structure including $ZnBr_2$ and a chiral amide based on (*R*,*R*)-1,2-diamminocyclohexane, a well known chiral building block.



(I)

In this paper the crystal structure of (*R*,*R*)-1,2-diacetamidocyclohexanedibromozinc(II) is described. The main interest in this study is in the ability of Zn to coordinate the amidic bond *via* its O atom in the sp^2 lone-pair direction. According to our hypothesis, amide bonds in a peptide backbone not engaged in intra- or interchain hydrogen bonds could coordinate metals like Zn. Detailed structural knowledge of a Zn–chiral-amide complex would help to clarify the strength of the interaction of Zn^{II} with peptides. Fig. 1 shows a fragment of the polymeric chain [(*R*,*R*)-1,2-diacetamidocyclohexanedibromozinc(II)]$_n$. The 1,2–Diacetamidocyclohexane (DCH) ligand acts as 1,8-bridging in the structure; it is coordinated by the O atom of each of its acetamide groups to the neighbouring Zn atom. The Zn$\cdots$Zn$''$ [symmetry code: ($''$) x, $1 + y$, z] distance is 7.496 (2) Å. The Zn atom is in a tetrahedral donor atom environment, which comprises two

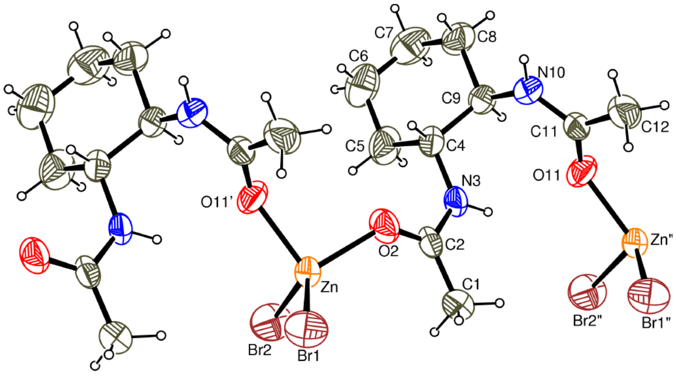


Figure 1

Perspective view of a fragment of the polymeric chain showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. [Symmetry codes: (′) *x*, 1 + *y*, *z*; (″) *x*, *y* − 1, *z*.]

bromide ions and two O atoms of two DCH ligands. The Zn—Br and Zn—O distances in the coordination polyhedron are 2.342 (1)/2.350 (1) and 1.970 (4)/1.974 (4) Å, respectively. The (*R*,*R*)-1,2-diacetamidocyclohexane adopts a chair conformation with the two acetamide groups in equatorial positions. There is one intramolecular hydrogen bond [N3—H3···O11 2.864 (6) Å and 127°] (Table 2). The crystal packing is characterized by several van der Waals contacts, the shortest being 3.620 (5) Å for Br2···N10‴ [symmetry code: (‴) *y* − 1, 1 − *x*, $z + \frac{1}{4}$]; these interactions result in chains parallel to the *b* axis.

Experimental

The title compound was prepared as follows: 1.98 g (0.01 mol) of (*R*,*R*)-1,2-diacetamidocyclohexane (Hirayama & Shibayama, 2001) was dissolved in 20 ml of glacial acetic acid. 2.25 g (0.01 mol) of anhydrous $ZnBr_2$ was added and dissolved by warming. After complete dissolution, 75% of the solvent was evaporated under reduced pressure. On standing for several days at room temperature, the oily residue deposited colourless crystals; they were filtered off and washed with ethyl acetate and diethyl ether.

Crystal data

$[ZnBr_2(C_{10}H_{18}N_2O_2)]$
$M_r = 423.45$
Tetragonal, $P4_3$
$a = 7.496$ (2) Å
$c = 27.941$ (5) Å
$V = 1570.0$ (7) Å^3
$Z = 4$
$D_x = 1.791$ Mg m^{-3}
$D_m = 1.78$ (2) Mg m^{-3}
D_m measured by flotation in CCl_4 and $C_2H_4Br_2$
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 6.5$–9.9°
$\mu = 6.65$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, colourless
0.40 × 0.38 × 0.28 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{min} = 0.086$, $T_{max} = 0.159$
4956 measured reflections
2335 independent reflections
1330 reflections with $I > 2\sigma(I)$
$R_{int} = 0.062$
$\theta_{max} = 30.0°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 39$
3 standard reflections
frequency: 1 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.076$
$S = 0.95$
2335 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.015 (15)

Table 1

Selected geometric parameters (Å, °).

Zn—O11	1.970 (4)	Zn···Zn″	7.496 (2)
Zn—O2′	1.974 (4)	O2—C2	1.237 (7)
Zn—Br1	2.3416 (11)	C11—O11	1.264 (7)
Zn—Br2	2.3495 (10)		
O11—Zn—O2′	95.67 (18)	O2′—Zn—Br2	108.47 (14)
O11—Zn—Br1	111.69 (13)	Br1—Zn—Br2	118.59 (4)
O2′—Zn—Br1	117.92 (14)	C2—O2—Zn″	132.1 (4)
O11—Zn—Br2	100.76 (14)	C11—O11—Zn	134.7 (4)

Symmetry codes: (′) *x*, *y* − 1, *z*; (″) *x*, 1 + *y*, *z*.

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O11	0.86	2.26	2.864 (6)	127

Although no Friedel pairs were measured, the value of the Flack (1983) parameter agrees with the absolute configuration deduced from the synthetic pathway. Inverting the configuration leads to a value of 0.98 (2).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *WinGX* (Version 1.63.02; Farrugia, 1999).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Bekaert, A., Barberan, O., Kaloun, E. B., Rabhi, C., Danan, A., Brion, J. D., Lemoine, P. & Viossat, B. (2002*a*). *Z. Kristallogr. New Cryst. Struct.* **217**, 128–130.

Bekaert, A., Barberan, O., Kaloun, E. B., Rabhi, C., Danan, A., Brion, J. D., Lemoine, P. & Viossat, B. (2002*b*). *Z. Kristallogr. New Cryst. Struct.* **217**, 507–509.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Enraf–Nonius (1994). *CAD-4 EXPRESS Software*. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.

Hirayama, N. & Shibayama, K. (2001). Jpn Patent No. 172.289 (26.06.2001), *Chem. Abstr.* (2001), **135**, 61143.

Ozutsumi, K., Koide, M., Suzuki, H. & Ishiguro, S. (1993). *J. Phys. Chem.* **97**, 500–502.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Suzuki, H., Fukushima, N., Ishiguro, S., Mazuda, H. & Ohtaki, H. (1991). *Acta Cryst.* C**47**, 1838–1842.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

Acta Cryst. (2003). E**59**, m574–m575 Alain Bekaert *et al.* • $[ZnBr_2(C_{10}H_{18}N_2O_2)]$ **m575**