

catena-Poly[[dibromozinc(II)]-di- μ -1,4-dioxan- κ^2 O:O']**John C. Barnes**Department of Chemistry, University of Dundee,
Perth Road, Dundee DD1 4HN, ScotlandCorrespondence e-mail:
j.c.barnes@dundee.ac.uk**Key indicators**Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
R factor = 0.041
wR factor = 0.106
Data-to-parameter ratio = 22.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $[\text{ZnBr}_2(\text{C}_4\text{H}_8\text{O}_2)]_n$ or $\text{ZnBr}_2 \cdot (\text{dioxan})$, has a zigzag chain structure in which the 1,4-dioxan molecules link tetrahedrally coordinated Zn atoms. Each dioxan ring sits on a centre of symmetry. The Zn—Br distances are 2.3110 (8) and 2.3169 (8) Å, and angle Br1—Zn1—Br2 is 124.53 (3)°. The Zn—O distances are 2.054 (4) and 2.043 (3) Å, and angle O—Zn—O is 89.6 (15)°.

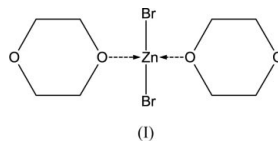
Received 4 June 2004

Accepted 9 June 2004

Online 19 June 2004

Comment

1,4-Dioxan forms crystalline adducts with a very wide range of metal halides, nitrates and perchlorates. Phase diagrams of ternary systems (metal halide–dioxan–water) by Lynch and co-workers (*e.g.* Weickel & Lynch, 1950; Schott & Lynch, 1966) show that there is competition between water and dioxan at 298 K. Some metals give a hydrate as the only solid product, others give only a dioxan adduct, and a third group form both of these together with ternary compounds.



Structural studies have shown that dioxan may be coordinated directly to a metal or may form hydrogen bonds with the H atoms of coordinated water molecules (*e.g.* Barnes & Weakley, 1976; Barnes, 2004a). The chair-shaped dioxan molecules cannot chelate. They almost invariably form 1,4-bridges in which each O atom usually coordinates to only one metal atom but may form one or two hydrogen bonds.

$\text{ZnCl}_2 \cdot 2(\text{dioxan})$ (Boardman *et al.*, 1983) has an unusual trigonal pyramidal chain structure which includes a monodentate dioxan. In the present work, we report the structure at 150 K of $\text{ZnBr}_2 \cdot (\text{dioxan})$, (I).

Fig. 1 shows that (I) consists of zigzag chains, parallel to c , in which dioxan molecules bridge tetrahedrally coordinated zinc atoms. The two independent dioxan molecules lie about the centres of inversion at $(\frac{1}{2}, 0, \frac{1}{2})$ for O1, C2 and C3, and at $(\frac{1}{2}, 0, 0)$ for O4, C5 and C6. Selected geometric parameters are given in Table 1. The Zn—Br distances are 2.3110 (8) and 2.3169 (8) Å. These are significantly shorter than those in $[\text{ZnBr}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot 2(1,8\text{-cineol})$ [2.360 (2) Å, also determined at 120 K (Barnes, 2004b)] and the room-temperature structures of K_2ZnBr_4 (2.405 Å; Fábry *et al.*, 1993) and $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$ (2.483 Å; Duhlev *et al.*, 1988).

The sums of covalent radii are Zn—Br = 2.45 Å and Zn—O = 1.97 Å, while the sums of ionic radii give Zn—Br = 2.78 Å and Zn—O 2.28 Å. These values suggest that the Zn—Br

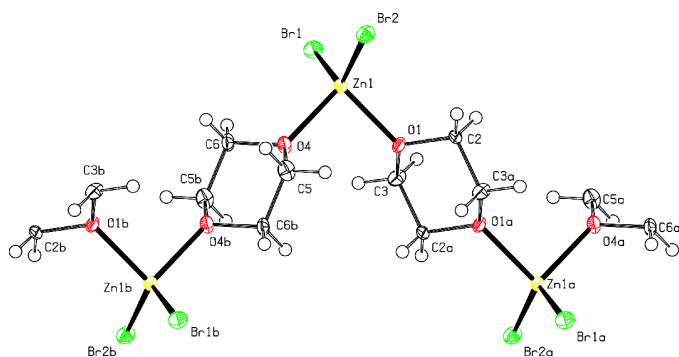


Figure 1
The structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. [Symmetry codes: (a) $1 - x, -y, 1 - z$; (b) $1 - x, -y, 2 - z$.]

interactions in all these compounds are largely covalent. The Zn—O distances in (I) [2.054 (4) and 2.043 (3) Å] are not significantly different from the Zn—OH₂ distances in [ZnBr₂(H₂O)₂] \cdot H₂O \cdot 2(1,8-cineol) and ZnBr₂ \cdot 2H₂O.

In (I), the torsion angles C3a—C2—O1—Zn1 [155.3 (2)°] and C5b—C6—O4—Zn1 [154.2 (2)°] show that the direction of the O—Zn vectors is close to equatorial rather than the equatorial/axial average often found in dioxan complexes of metal salts (Barnes & Weakley, 1976). Each of the fragments Zn1—O1 \cdots O1a—Zn1a and Zn1—O4 \cdots O4b—Zn1b has a torsion angle of 180° [symmetry codes: (a) $1 - x, -y, 1 - z$; (b) $1 - x, -y, 2 - z$]. The angle between the planes C2/C2a/C3/C3a and C5/C5b/C6/C6b is only 25.2 (4)°. Taken together, these factors produce a very compact zigzag chain structure, which minimizes steric hindrance between the dioxan molecules at the Zn atom. This allows the O—Zn—O angle to be only 89.6 (15)° and so provides space for the unusually close approach of the Br atoms to the zinc, and the large Br1—Zn1—Br2 angle of 124.53 (3)°.

Experimental

Crystals of (I) were obtained by slow evaporation of a solution of ZnBr₂ in dioxan at room temperature, under anhydrous conditions.

Crystal data

[ZnBr ₂ (C ₄ H ₈ O ₂)]	$D_x = 2.499 \text{ Mg m}^{-3}$
$M_r = 313.29$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2831 reflections
$a = 7.1326 (2) \text{ \AA}$	$\theta = 1.9\text{--}27.5^\circ$
$b = 12.0376 (4) \text{ \AA}$	$\mu = 12.48 \text{ mm}^{-1}$
$c = 9.8312 (3) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 99.4200 (14)^\circ$	Block, colourless
$V = 832.72 (4) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	1885 independent reflections
ϕ and ω cans	1606 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.052, T_{\text{max}} = 0.083$	$\theta_{\text{max}} = 27.5^\circ$
2831 measured reflections	$h = -9 \rightarrow 8$
	$k = -15 \rightarrow 12$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 3.2775P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 1.37 \text{ e \AA}^{-3}$
1885 reflections	$\Delta\rho_{\text{min}} = -0.96 \text{ e \AA}^{-3}$
83 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0142 (10)

Table 1

Selected geometric parameters (Å, °).

Zn1—O1	2.043 (3)	Zn1—Br1	2.3110 (8)
Zn1—O4	2.054 (4)	Zn1—Br2	2.3169 (8)
O1—Zn1—O4	89.60 (15)	Br1—Zn1—Br2	124.53 (3)
O1—Zn1—Br1	111.75 (11)	C3—O1—Zn1	117.8 (3)
O4—Zn1—Br1	106.06 (10)	C2—O1—Zn1	122.1 (3)
O1—Zn1—Br2	107.24 (10)	C5—O4—Zn1	119.1 (3)
O4—Zn1—Br2	112.16 (11)	C6—O4—Zn1	121.9 (3)

The H atoms were included in calculated positions and treated as riding atoms; C—H = 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{parent C atom})$. The highest peak lies on the Zn1—Br1 vector, 1.11 Å from Zn1.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1999); software used to prepare material for publication: SHELXL97.

We thank the EPSRC and Professor M. B. Hursthouse for collection of data at Southampton University.

References

- Barnes, J. C. (2004a). In preparation.
- Barnes, J. C. (2004b). Private communication to the Cambridge Structural Database, deposition number CCDC-240396. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Barnes, J. C. & Weakley, T. J. R. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1786–1790.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Boardman, A., Small, R. W. H. & Worrall, I. J. (1983). *Acta Cryst.* **C39**, 1005–1007.
- Duhlev, R., Brown, I. D. & Fassiani, R. (1988). *Acta Cryst.* **C44**, 1696–1698.
- Fábry, J., Breczewski, T., Zúñiga, F. J. & Arnaiz, A. R. (1993). *Acta Cryst.* **C49**, 946–950.
- Hooft, R. (1998). COLLECT. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Schott, H. & Lynch, C. C. (1966). *J. Chem. Eng. Data*, **11**, 215–224.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Spek, A. L. (1999). PLATON. University of Utrecht, The Netherlands.
- Weicksel, J. A. & Lynch, C. C. (1950). *J. Am. Chem. Soc.* **72**, 2632–2639.

supporting information

Acta Cryst. (2004). E60, m971–m972 [https://doi.org/10.1107/S1600536804014072]

catena-Poly[[dibromozinc(II)]-di- μ -1,4-dioxan- κ^2 O:O']

John C. Barnes

catena-Poly[[dibromozinc(II)]-di- μ -1,4-dioxan- κ^2 O:O']

Crystal data

[ZnBr₂(C₄H₈O₂)]

$M_r = 313.29$

Monoclinic, $P2_1/n$

$a = 7.1326$ (2) Å

$b = 12.0376$ (4) Å

$c = 9.8312$ (3) Å

$\beta = 99.4200$ (14)°

$V = 832.72$ (4) Å³

$Z = 4$

$F(000) = 592$

$D_x = 2.499$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71074$ Å

Cell parameters from 2831 reflections

$\theta = 1.9$ – 27.5°

$\mu = 12.48$ mm⁻¹

$T = 150$ K

Block, colourless

0.30 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer

Radiation source: Enraf–Nonius FR591 rotating anode

Graphite monochromator

Detector resolution: 9.091 pixels mm⁻¹

φ and ω scans to fill Ewald sphere

Absorption correction: multi-scan (SORTAV; Blessing, 1995)

$T_{\min} = 0.052$, $T_{\max} = 0.083$

2831 measured reflections

1885 independent reflections

1606 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -9 \rightarrow 8$

$k = -15 \rightarrow 12$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.106$

$S = 1.10$

1885 reflections

83 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 3.2775P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.37$ e Å⁻³

$\Delta\rho_{\min} = -0.96$ e Å⁻³

Extinction correction: SHELXL97,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0142 (10)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger. Hydrogen atoms were placed on calculated positions, riding on the adjacent carbon atom. Isotropic displacement parameters were set at 1.3 times that of the carbon atom.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.34430 (9)	0.17978 (5)	0.73063 (6)	0.0129 (2)
Br1	0.01610 (8)	0.17948 (5)	0.70049 (6)	0.0197 (2)
Br2	0.53024 (8)	0.33850 (4)	0.74508 (6)	0.0195 (2)
O1	0.4446 (5)	0.0740 (3)	0.5968 (4)	0.0151 (8)
C2	0.5349 (8)	0.1139 (4)	0.4840 (5)	0.0157 (11)
H2A	0.6085	0.1822	0.5125	0.020*
H2B	0.4370	0.1322	0.4037	0.020*
C3	0.3348 (8)	-0.0253 (4)	0.5548 (6)	0.0195 (11)
H3A	0.2350	-0.0083	0.4751	0.025*
H3B	0.2721	-0.0519	0.6315	0.025*
O4	0.4332 (5)	0.0709 (3)	0.8889 (4)	0.0162 (8)
C5	0.6330 (8)	0.0636 (5)	0.9438 (6)	0.0201 (12)
H5A	0.6668	0.1205	1.0164	0.026*
H5B	0.7084	0.0781	0.8696	0.026*
C6	0.3207 (8)	0.0493 (5)	0.9969 (5)	0.0176 (11)
H6A	0.1837	0.0536	0.9582	0.023*
H6B	0.3488	0.1061	1.0702	0.023*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0157 (4)	0.0123 (3)	0.0112 (3)	0.0014 (2)	0.0032 (2)	0.0000 (2)
Br1	0.0155 (3)	0.0209 (3)	0.0223 (3)	0.0015 (2)	0.0017 (2)	-0.0004 (2)
Br2	0.0205 (3)	0.0157 (3)	0.0233 (3)	-0.0032 (2)	0.0065 (2)	-0.0037 (2)
O1	0.020 (2)	0.0121 (17)	0.0149 (18)	-0.0021 (15)	0.0093 (16)	-0.0031 (14)
C2	0.027 (3)	0.008 (2)	0.015 (2)	-0.001 (2)	0.010 (2)	0.0021 (19)
C3	0.021 (3)	0.011 (2)	0.028 (3)	-0.006 (2)	0.013 (2)	-0.004 (2)
O4	0.0129 (18)	0.023 (2)	0.0129 (17)	0.0026 (15)	0.0031 (14)	0.0043 (15)
C5	0.013 (3)	0.027 (3)	0.021 (3)	-0.002 (2)	0.003 (2)	0.004 (2)
C6	0.018 (3)	0.023 (3)	0.014 (3)	0.004 (2)	0.008 (2)	0.005 (2)

Geometric parameters (Å, °)

Zn1—O1	2.043 (3)	C3—H3A	0.9900
Zn1—O4	2.054 (4)	C3—H3B	0.9900
Zn1—Br1	2.3110 (8)	O4—C5	1.442 (7)
Zn1—Br2	2.3169 (8)	O4—C6	1.454 (6)
O1—C3	1.451 (6)	C5—C6 ⁱⁱ	1.495 (8)
O1—C2	1.452 (6)	C5—H5A	0.9900
C2—C3 ⁱ	1.504 (7)	C5—H5B	0.9900
C2—H2A	0.9900	C6—H6A	0.9900
C2—H2B	0.9900	C6—H6B	0.9900
O1—Zn1—O4	89.60 (15)	O1—C3—H3B	109.8
O1—Zn1—Br1	111.75 (11)	C2 ⁱ —C3—H3B	109.8
O4—Zn1—Br1	106.06 (10)	H3A—C3—H3B	108.3
O1—Zn1—Br2	107.24 (10)	C5—O4—C6	110.2 (4)
O4—Zn1—Br2	112.16 (11)	C5—O4—Zn1	119.1 (3)
Br1—Zn1—Br2	124.53 (3)	C6—O4—Zn1	121.9 (3)
C3—O1—C2	110.0 (4)	O4—C5—C6 ⁱⁱ	110.1 (5)
C3—O1—Zn1	117.8 (3)	O4—C5—H5A	109.6
C2—O1—Zn1	122.1 (3)	C6 ⁱⁱ —C5—H5A	109.6
O1—C2—C3 ⁱ	109.2 (4)	O4—C5—H5B	109.6
O1—C2—H2A	109.8	C6 ⁱⁱ —C5—H5B	109.6
C3 ⁱ —C2—H2A	109.8	H5A—C5—H5B	108.2
O1—C2—H2B	109.8	O4—C6—C5 ⁱⁱ	109.5 (4)
C3 ⁱ —C2—H2B	109.8	O4—C6—H6A	109.8
H2A—C2—H2B	108.3	C5 ⁱⁱ —C6—H6A	109.8
O1—C3—C2 ⁱ	109.2 (4)	O4—C6—H6B	109.8
O1—C3—H3A	109.8	C5 ⁱⁱ —C6—H6B	109.8
C2 ⁱ —C3—H3A	109.8	H6A—C6—H6B	108.2

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