metal-organic compounds

catena-Poly[dibromozinc(II)-μ-ethylenediamine-N:N']: resolution of structural anomalies resulting from the interpretation of vibrational spectra

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The title structure, $[ZnBr_2(C_2H_8N_2)]$, is made up of infinite $-ZnBr_2-(en)-ZnBr_2-(en)-$ zigzag chains. Each repeat unit contains a *trans* ethylenediamine ligand $[N-C-C-N -179 (1)°]$, which bridges two approximately tetrahedral but crystallographically distinct Zn atoms. One Zn atom is bisected by a crystallographic twofold axis, whereas the other has mirror symmetry. Even though the crystal packing does not allow significant interaction between Zn and N atoms on adjacent chains, it does facilitate extensive intermolecular N—H⋯Br hydrogen bonding (N⋯H 2.69–2.96 Å).

Comment

Prior to the present work, the only structural information concerning monoethylenediamine zinc dihalides had been obtained from vibrational spectroscopy. Raman and IR studies of $Zn(en)Cl_2$ (en is ethylenediamine) carried out by Newman & Powell (1961) and Krishnan & Plane (1966) indicated that the solid consists of infinite chains of Zn atoms bridged by en ligands, with N atoms *trans* to the C—C bond. The same studies concluded that both Cl atoms are attached to Zn, presumably completing a tetrahedral arrangement of bonds, *cf.* the crystal structure of *catena*-(μ-2-ethylenediamine)mercury(II) dibromide (Matkovic-Calogovic & Sikirica, 1990), in which a cationic $-(en)-Hg-(en)-Hg-$ polymeric chain is accompanied by Br^- anions. Repetition of the $Zn(en)Cl_2$ work and its extension to $Zn(en)Br_2$ by Iwamoto & Shriver (1971) indicated that both structures consist of polymeric $Zn(en)X_2$ chains but, because of the complexity of the spectra, it was thought that the en moiety was probably in sites of low symmetry. More recent work by Bennett *et al.* (1990) also explained the vibrational spectra in terms of $-ZnX_2-(en)-ZnX_2-(en)-$ polymeric chains, but with en in its symmetric *trans* form; however, they concluded that there was additional interaction between Zn and NH_2 groups on neighbouring

molecules, leading to an effective octahedral coordination around Zn.

The structure of the title molecule, (I), reported herein confirms the existence of polymeric $-ZnBr_2-(en)-ZnBr_2-(en)-$ chains and a *trans* en conformation, but rules out intermolecular $NH_2\cdots Zn$ contacts. Despite the en ligand

(I)
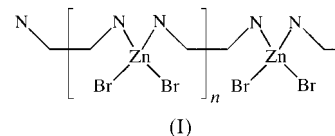
having a *trans* conformation, its two N atoms are attached to Zn centres with different crystallographic symmetry and significantly different geometry, *e.g.* $N1-Zn1-N1^i$ 98.6 (8)° (mirror symmetry) and $N2-Zn2-N2^{ii}$ 111.6 (10)° (twofold axis) [symmetry codes: (i) $\frac{1}{2} - x, y, z$; (ii) $1 - x, -y, z$]. The complexity of the vibrational spectra can therefore be related to asymmetric NH_2 environments.

Interestingly, $-HgI_2-(en)-HgI_2-(en)-$ (Matkovic-Calogovic & Sikirica, 1990), the only other zinc $M(en)X_2$ complex to be characterized by single-crystal methods, also consists of zigzag chains, but in this case each en is centrosymmetric and hence crystallographically constrained to be *trans*.
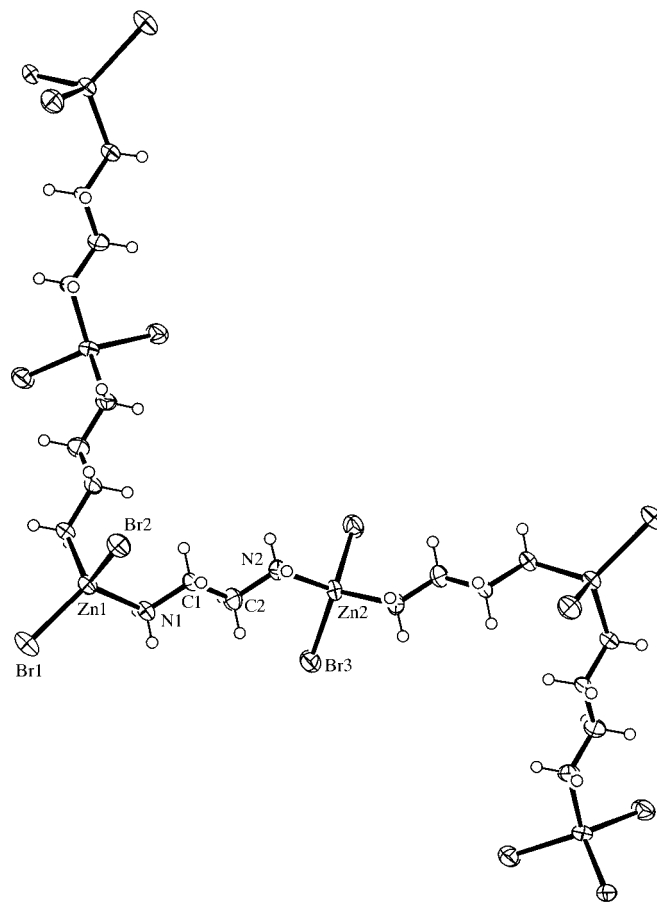

Figure 1
A molecular view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

Suitable crystals of (I) were prepared by slow evaporation of a mixture of $ZnCl_2$ (1 ml, 0.2 M) and en (1 ml, 0.2 M), both in methanol, to which two drops of 35% w/w hydrogen peroxide had been added.

Crystal data

$[ZnBr_2(C_2H_8N_2)]$	Cu $K\alpha$ radiation
$M_r = 285.29$	Cell parameters from 25
Orthorhombic, $Ima2$	reflections
$a = 19.270\ (4)$ Å	$\theta = 8.3–16.2°$
$b = 7.2111\ (17)$ Å	$\mu = 17.47$ mm^{-1}
$c = 10.025\ (5)$ Å	$T = 293\ (2)$ K
$V = 1393.1\ (8)$ Å^3	Needle, colourless
$Z = 8$	$0.25 \times 0.15 \times 0.10$ mm
$D_x = 2.721$ Mg m^{-3}	

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.075$
$\omega/2\theta$ scans	$\theta_{max} = 64.98°$
Absorption correction: ψ scan	$h = 0 \rightarrow 22$
(North et al., 1968)	$k = -8 \rightarrow 8$
$T_{min} = 0.062$, $T_{max} = 0.174$	$l = 0 \rightarrow 11$
1206 measured reflections	3 standard reflections
631 independent reflections	every 150 reflections
565 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F) = 0.053$	$\Delta\rho_{max} = 1.22$ e Å^{-3}
$wR(F^2) = 0.151$	$\Delta\rho_{min} = -1.44$ e Å^{-3}
$S = 1.019$	Extinction correction: SHELXL97
631 reflections	(Sheldrick, 1997)
70 parameters	Extinction coefficient: 0.00034 (4)
H-atom parameters constrained	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.1171P)^2]$	Flack parameter = 0.12 (14)
where $P = (F_o^2 + 2F_c^2)/3$	

H atoms were constrained to chemically reasonable positions (C—H = 0.97 Å).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985b); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 1
Selected geometric parameters (Å, °).

Br1—Zn1	2.369 (4)	Zn2—N2	2.063 (14)
Br2—Zn1	2.399 (5)	N1—C1	1.47 (2)
Br3—Zn2	2.386 (3)	N2—C2	1.49 (2)
Zn1—N1	2.053 (14)	C1—C2	1.50 (2)
N1—Zn1—N1^i	98.6 (8)	N2^{ii}—Zn2—N2	111.6 (10)
N1—Zn1—Br1	118.0 (4)	N2^{ii}—Zn2—Br3	109.0 (4)
N1—Zn1—Br2	108.9 (4)	N2—Zn2—Br3	106.3 (4)
Br1—Zn1—Br2	104.2 (2)	Br3—Zn2—Br3^{ii}	114.9 (2)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1A$\cdots$Br3^{iii}	0.90	2.69	3.44 (1)	142
N1—H1B$\cdots$Br1^{iv}	0.90	2.73	3.56 (2)	154
N2—H2A$\cdots$Br3^v	0.90	2.96	3.65 (2)	135
N2—H2B$\cdots$Br2^{vi}	0.90	2.89	3.69 (1)	149

Symmetry codes: (iii) $1 - x, \frac{1}{2} + y, z - \frac{1}{2}$; (iv) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (v) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1500). Services for accessing these data are described at the back of the journal.

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