

Poly[[bis[(dimethyl sulfoxide)zinc(II)]-di- $\mu_4$ -benzene-1,4-dicarboxylato] dimethyl sulfoxide pentasolvate]Shi-Yao Yang,<sup>a</sup> La-Sheng Long,<sup>a</sup>  
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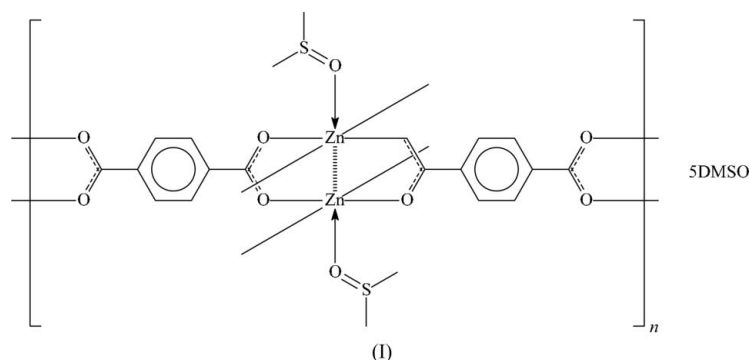
## Key indicators

Single-crystal X-ray study  
 $T = 173$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
Disorder in main residue  
 $R$  factor = 0.045  
 $wR$  factor = 0.121  
Data-to-parameter ratio = 18.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

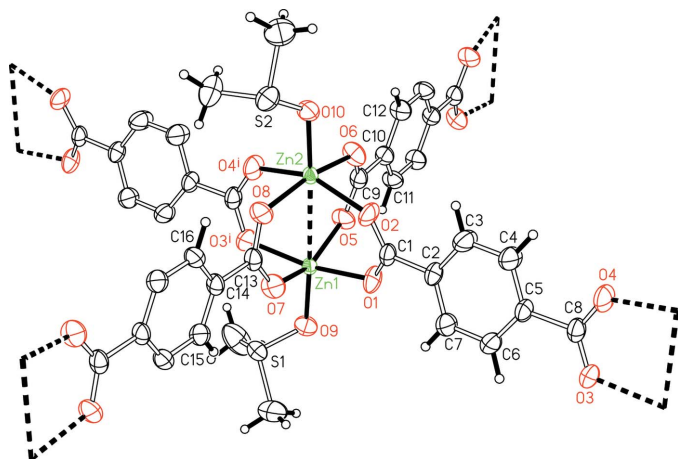
In the crystal structure of the title compound,  $[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_2\text{H}_6\text{OS})_2] \cdot 5\text{C}_2\text{H}_6\text{OS}$ , four independent carboxylate units of the 1,4-benzenedicarboxylate groups chelate to two Zn atoms to give rise to  $-\text{O}-\text{C}-\text{O}-\text{Zn} \cdots \text{Zn}-$  rings, the four O atoms around each zinc atom forming a square, above which is a dimethyl sulfoxide (DMSO) molecule and below which is the other Zn atom. The bridging mode of the 1,4-benzenedicarboxylate groups, one of which lies on a general position and the other two on inversion centers, leads to a layer structure having DMSO molecules between the layers. The uncoordinated solvent molecules account for about 80% of the volume of the unit cell.

## Comment

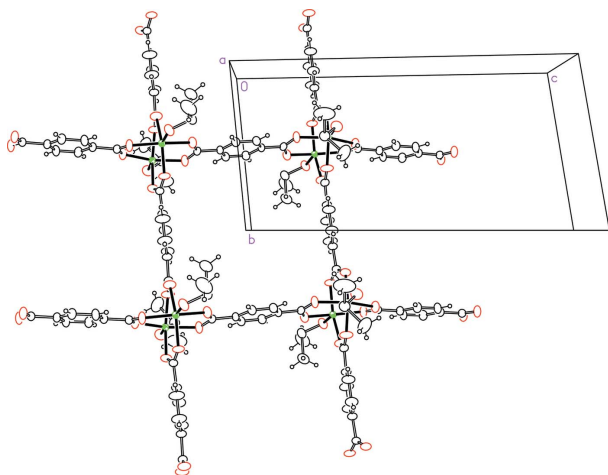
The product of the hydrothermal reaction of a zinc salt and sodium 1,4-benzenedicarboxylate is a polymeric water-coordinated zinc 1,4-benzenedicarboxylate (Yang *et al.*, 2001). Under non-hydrothermal conditions, a solvent such as dimethylformamide (DMF) must be used to dissolve the reactants; however, the use of DMF leads to a co-crystal of this compound with sodium 1,4-benzenedicarboxylate. DMF is also incorporated into the crystal structure (Yang *et al.*, 2002). A study on the crystallization of zinc 1,4-benzenedicarboxylates has also reported that the DMF adduct absorbs small molecules (Edgar *et al.*, 2001) so that these compounds can be classified as open framework compounds (Li *et al.*, 1998). The present synthesis uses dimethyl sulfoxide (DMSO) as solvent in place of DMF and is an extension of the study on tris-(1,4-benzenedicarboxylato)tetrakis(dimethyl sulfoxide)dihydroxotetrazinc(II) (Wang *et al.*, 2001).



In the crystal structure of the title compound, (I) (Fig. 1), one of the 1,4-benzenedicarboxylate groups lies on a general position and two lie on centers of inversion. The four independent carboxylate units of these groups chelate to the two Zn atoms to form an  $-\text{O}-\text{C}-\text{O}-\text{Zn} \cdots \text{Zn}-$  ring  $[\text{Zn} \cdots \text{Zn}$



**Figure 1**  
ORTEP plot (Johnson, 1976) of the polymeric title structure. Displacement ellipsoids are drawn at the 70% probability level and H atoms as spheres of arbitrary radii. The uncoordinated DMSO molecules are not shown. [Symmetry code: (i)  $x, 1 + y, z$ .]



**Figure 2**  
ORTEP plot (Johnson, 1976) of the layer structure of (I). The uncoordinated DMSO molecules and the second disorder component are not shown.

$= 2.9473(4) \text{ \AA}$ ]. The four O atoms around each Zn atom form a square above which is a DMSO molecule; if the other Zn atom below is not considered to be bonded, then the geometry is square pyramidal. As the axes of the two rigid 1,4-benzenedicarboxylate groups are aligned at approximately  $90^\circ$  to each other, the polymeric structure has a layer formation. The uncoordinated DMSO molecules occupy the space between the layers, and some also protrude into the layers. According to *PLATON* (Spek, 2003), the ordered and disordered uncoordinated solvent molecules account for about 80% of the volume of the unit-cell contents. This feature explains the ready loss of solvent when the crystals are exposed to air.

There is a small number of structurally authenticated examples of tetrakis( $\mu_2$ -carboxylato)bis[*N*-heterocyclezinc] adducts, e.g. tetrakis( $\mu_2$ -acetato)bis(pyridinezinc) (Singh *et al.*, 1997); however, the *O*-donor adducts appear to be limited to the 1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indole-3-

acetate adducts with *N,N*-dimethylacetamide and 1-methylpyrrolidinone only (Zhou *et al.*, 2000). The title compound is another example of such an *O*-donor adduct, but its structure is exceptional in view of the extremely large space occupied by solvent molecules.

## Experimental

The title compound was obtained by using a layer diffusion method. Zinc nitrate hexahydrate (0.059 g, 0.20 mmol) and 1,4-benzenedicarboxylic acid (0.033 g, 0.20 mmol) were dissolved in DMSO (5 ml) and the solution was placed in a test tube. Tributylamine (0.037 g, 0.20 mmol) dissolved in DMSO (5 ml) was added so as not to agitate the bottom layer. The tube was covered and set aside for a month. Colorless needle-shaped crystals formed on the walls of the tube.

### Crystal data

$[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_2\text{H}_6\text{OS})_2] \cdot 5\text{C}_2\text{H}_6\text{OS}$   
 $M_r = 1005.86$   
 Triclinic,  $P\bar{1}$   
 $a = 10.4449(4) \text{ \AA}$   
 $b = 10.9120(5) \text{ \AA}$   
 $c = 20.9707(9) \text{ \AA}$   
 $\alpha = 81.311(1)^\circ$   
 $\beta = 80.278(1)^\circ$   
 $\gamma = 73.004(1)^\circ$   
 $V = 2239.8(2) \text{ \AA}^3$

$Z = 2$   
 $D_x = 1.491 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 7024 reflections  
 $\theta = 2.4\text{--}28.1^\circ$   
 $\mu = 1.46 \text{ mm}^{-1}$   
 $T = 173(2) \text{ K}$   
 Column, colorless  
 $0.40 \times 0.33 \times 0.27 \text{ mm}$

### Data collection

Bruker APEX area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Bruker, 2002)  
 $T_{\min} = 0.546, T_{\max} = 0.674$   
 25259 measured reflections

9977 independent reflections  
 9104 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -13 \rightarrow 13$   
 $l = -26 \rightarrow 27$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.121$   
 $S = 1.00$   
 9977 reflections  
 530 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 4.2336P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.47 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.95 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Zn1—O1	2.018 (2)	Zn2—O2	2.044 (2)
Zn1—O3 <sup>i</sup>	2.036 (2)	Zn2—O4 <sup>i</sup>	2.056 (2)
Zn1—O5	2.040 (2)	Zn2—O6	2.012 (2)
Zn1—O7	2.051 (2)	Zn2—O8	2.029 (2)
Zn1—O10	1.970 (2)	Zn2—O9	1.981 (2)
O1—Zn1—O3 <sup>i</sup>	165.5 (1)	O2—Zn2—O4 <sup>i</sup>	152.7 (1)
O1—Zn1—O5	89.6 (1)	O2—Zn2—O6	88.9 (1)
O1—Zn1—O7	87.2 (1)	O2—Zn2—O8	90.1 (1)
O1—Zn1—O10	98.0 (1)	O2—Zn2—O9	105.2 (1)
O3 <sup>i</sup> —Zn1—O5	89.6 (1)	O4 <sup>i</sup> —Zn2—O6	87.8 (1)
O3 <sup>i</sup> —Zn1—O7	86.8 (1)	O4 <sup>i</sup> —Zn2—O8	86.7 (1)
O3 <sup>i</sup> —Zn1—O10	96.0 (1)	O4 <sup>i</sup> —Zn2—O9	102.1 (1)
O5—Zn1—O7	152.1 (1)	O6—Zn2—O8	165.8 (1)
O5—Zn1—O10	107.0 (1)	O6—Zn2—O9	98.0 (1)
O7—Zn1—O10	100.8 (1)	O8—Zn2—O9	96.0 (1)

Symmetry code: (i)  $x, y + 1, z$ .

The structure is disordered in four of the seven DMSO molecules, the four being the molecules having atoms S2, S3, S4 and S5. One of the two DMSO molecules that are engaged in coordination is also disordered. These four are disordered over two positions each, such that the molecule shares its O and two C atoms; one sulfur component lies above and the other below the C–C–O triangle. For the four, the S–O distances were restrained to 1.50 (1) Å and the S–C distances to 1.81 (1) Å. The displacements of the minor (primed) S atoms were restrained to be nearly isotropic. The occupancies of the major components refined to S2 0.88 (1), S3 0.63 (1), S4 0.91 (1) and S5 0.94 (1). The final difference Fourier map had a peak of  $1.5 e \text{ \AA}^{-3}$  at about 1 Å from atom S6, but an attempt to refine the peak as a disorder component did not lead to any meaningful outcome. The disorder also affected the aromatic rings and the C–C distances in the rings were restrained to 1.39 (1) Å. H atoms were placed at calculated positions [C–H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the aromatic H atoms, and C–H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the aliphatic H atoms] and included in the refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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