

[1,2-Bis(methylthio)ethane- $\kappa^2S,S'$ ]dichlorozinc(II)

Masood Parvez,\* Peter D. Clark and Hong Yao

Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4

Correspondence e-mail: parvez@ucalgary.ca

Received 24 April 2003

Accepted 30 April 2003

Online 9 May 2003

## Key indicators

Single-crystal X-ray study

T = 170 K

Mean  $\sigma(C-C)$  = 0.009 Å

R factor = 0.040

wR factor = 0.117

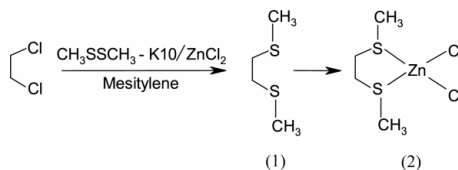
Data-to-parameter ratio = 20.3

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

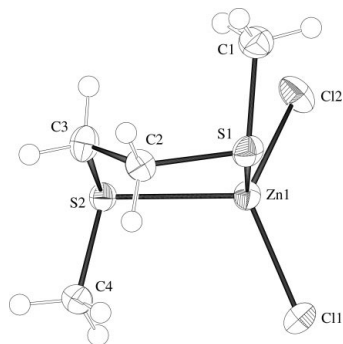
The central Zn atom in the structure of the title compound,  $[ZnCl_2(C_4H_{10}S_2)]$ , exhibits a distorted tetrahedral geometry and is coordinated by two Cl and two S atoms, with Zn–Cl distances of 2.203 (2) and 2.212 (2) Å, and Zn–S distances of 2.390 (2) and 2.459 (2) Å. The angles Cl–Zn–Cl and S–Zn–S are 123.28 (7) and 90.68 (6)°, respectively, while the Cl–Zn–S angles are in the range 106.13 (6)–112.69 (7)°.

## Comment

Dithio compounds are of considerable interest with respect to their use in preparing conducting materials from organic substrates and for chelation of metal species. In this paper, we report a rather unusual preparation of [1,2-bis(methylthio)ethane]dichlorozinc(II), (2), from the commonly available solvent 1,2-dichloroethane and dimethyl disulfide (DMDS), using a  $ZnCl_2$ -impregnated montmorillonite clay. Previously (Clark *et al.*, 1996), we have reported the use of such clay materials to catalyse the electrophilic substitution of aromatics by –SMe groups. The mechanism of these reactions likely occurs by coordination of one S atom of DMDS to the  $ZnCl_2$  adsorbed on the clay surface, rendering the other S atom of DMDS electrophilic, followed by attack of the aromatic at that electrophilic sulfur. In the present case of the formation of (2), it is probable that the Cl of the dichloroethane solvent coordinates at the  $ZnCl_2$  adsorbed at the clay surface, followed by attack of DMDS at the now electrophilic carbon bonded to the adsorbed Cl. A repeat of this process at the second C–Cl center results in the dithio compound (1), which then is able to chelate the  $ZnCl_2$  to form complex (2).



The crystal structure is composed of discrete monomeric molecules of (2) (Fig. 1) separated by normal van der Waals distances. The Zn atom is coordinated by two Cl and two S atoms, with Zn–Cl distances of 2.203 (2) and 2.212 (2) Å, and Zn–S distances of 2.390 (2) and 2.459 (2) Å. The angles Cl–Zn–Cl and S–Zn–S are 123.28 (7) and 90.68 (6)°, respectively, while the angles Cl–Zn–S are in the range 106.13 (6)–112.69 (7)°. The geometry around the Zn atom is distorted tetrahedral. A similar distorted tetrahedral geometry has been reported for the structures of (*N,N'*-dimethyldithiooxamide)-dichlorozinc(II) (Antolini *et al.*, 1987), *trans*-[2,3-bis(methyl-



**Figure 1**  
ORTEP (Johnson, 1976) drawing of (2), with displacement ellipsoids drawn at the 50% probability level.

thio)hexane-*S,S'*]dichlorozinc(II) (Parvez *et al.*, 1997), *trans*-[1,2-bis(methylthio)cyclohexane-*S,S'*]dichlorozinc(II) (Parvez *et al.*, 1997) and *cis*-[5,6-bis(methylthio)-1,3-cycloheptadiene-*S,S'*]dichlorozinc(II) (Parvez *et al.*, 1997).

The S–C distances in (2) range between 1.801 (7) and 1.828 (6) Å, in agreement with reported mean values (Orpen *et al.*, 1994). The Zn1/S1/S2/C2/C3 five-membered ring adopts a C3-envelope conformation, with C3 0.587 (9) Å out of the plane formed by the rest of the atoms in the ring; the maximum deviation of any atom from the mean plane is 0.098 (2) Å.

## Experimental

DMDS (5.64 g, 0.06 mol) was added to a stirred mixture of mesitylene (1.2 g, 0.01 mol) and K10/ZnCl<sub>2</sub> (5 wt% ZnCl<sub>2</sub>) (10 g) (Clark *et al.*, 1994) in dichloroethane (40 ml). After heating the mixture under reflux for 18 h, the reaction mixture was cooled and the clay catalyst was removed by filtration. Evaporation of the dichloroethane, mesitylene and excess DMDS left a semi-solid residue, which afforded colorless crystals of (2) on crystallization from ethanol [m.p. > 373 K (decomposition)].

### Crystal data

[ZnCl <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> S <sub>2</sub> )]	$D_x = 1.779 \text{ Mg m}^{-3}$
$M_r = 258.51$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 7.3110 (14) \text{ \AA}$	$\theta = 10.0\text{--}15.0^\circ$
$b = 17.5535 (15) \text{ \AA}$	$\mu = 3.45 \text{ mm}^{-1}$
$c = 7.7836 (15) \text{ \AA}$	$T = 170 (2) \text{ K}$
$\beta = 104.984 (14)^\circ$	Prism, colorless
$V = 964.9 (3) \text{ \AA}^3$	$0.35 \times 0.26 \times 0.15 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku AFC-6S diffractometer	$R_{\text{int}} = 0.066$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: $\psi$ scan	$h = 0 \rightarrow 8$
(North <i>et al.</i> , 1968)	$k = 0 \rightarrow 20$
$T_{\text{min}} = 0.378$ , $T_{\text{max}} = 0.625$	$l = -9 \rightarrow 8$
1834 measured reflections	3 standard reflections
1706 independent reflections	every 200 reflections
1123 reflections with $I > 2\sigma(I)$	intensity decay: 4.9%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 1.42P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.117$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
1706 reflections	$\Delta\rho_{\text{min}} = -0.80 \text{ e \AA}^{-3}$
84 parameters	H-atom parameters constrained

**Table 1**

Selected geometric parameters (Å, °).

Zn1–Cl2	2.203 (2)	S1–C1	1.813 (7)
Zn1–Cl1	2.212 (2)	S1–C2	1.828 (6)
Zn1–S2	2.390 (2)	S2–C4	1.801 (7)
Zn1–S1	2.459 (2)	S2–C3	1.809 (7)
Cl2–Zn1–Cl1	123.28 (7)	C1–S1–C2	102.3 (3)
Cl2–Zn1–S2	112.21 (7)	C1–S1–Zn1	103.8 (2)
Cl1–Zn1–S2	112.69 (7)	C2–S1–Zn1	97.8 (2)
Cl2–Zn1–S1	106.14 (7)	C4–S2–C3	102.3 (3)
Cl1–Zn1–S1	106.13 (6)	C4–S2–Zn1	104.1 (2)
S2–Zn1–S1	90.68 (6)	C3–S2–Zn1	99.4 (2)

The H atoms were located in a difference Fourier map and were included in the refinement at idealized positions, with isotropic displacement parameters 1.5 (CH<sub>3</sub>) and 1.2 (CH<sub>2</sub>) times  $U_{\text{eq}}(\text{C})$ , with C–H distances of 0.98 and 0.99 Å, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

## References

- Antolini, L., Fabretti, A. C., Franchini, G., Menabue, L., Pellacani, G. C., Desseyn, H. O., Dommissie, R. & Hofmans, H. C. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1921–1928.
- Clark, J. H., Cullen, S. R., Barlow, S. J. & Bastock, T. W. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 1117–1130.
- Clark, P. D., Mesher, S. T. E. & Primak, A. (1996). *Phosphorus Sulfur Silicon*, **114**, 99–107.
- Fan, H.-F. (1991). *SAPI91*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1994). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi and J. D. Dunitz, pp. 751–858. New York: VCH.
- Parvez, M., Mesher, S. T. E. & Clark, P. D. (1997). *Acta Cryst.* **C53**, 681–685.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.