

## Bis(thiosemicarbazide)zinc(II) bis(maleate) dihydrate. Erratum

Sheng-Li Li,<sup>a</sup> Jie-Ying Wu,<sup>a</sup>  
Yu-Peng Tian,<sup>a</sup> Hoong-Kun Fun<sup>b\*</sup>  
and Suchada Chantrapromma<sup>c\*</sup>

<sup>a</sup>Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China, <sup>b</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and <sup>c</sup>Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand

Correspondence e-mail: hkfun@usm.my,  
suchada.c@psu.ac.th

In the paper by Li, Wu, Tian, Fun & Chantrapromma [*Acta Cryst.* (2005), E61, m2701–m2703], there is an error with regard to the symmetry-code identifiers in the fourth paragraph of the *Comment*. The corrected sentence is ‘The N1–H1N1···O3, N1–H2N1···S1<sup>ii</sup>, N2–H1N2···O1<sup>iii</sup>, N3–H1N3···O2<sup>iii</sup> and N3–H2N3···O1<sup>iv</sup> hydrogen bonds (see Table 2 for symmetry codes) link the complex cations and maleate anions into sheets parallel to the (10 $\bar{2}$ ) plane (Fig. 2)’.

Received 6 December 2005

Accepted 8 December 2005

Online 16 December 2005

Sheng-Li Li,<sup>a</sup> Jie-Ying Wu,<sup>a</sup>  
Yu-Peng Tian,<sup>a</sup> Hoong-Kun Fun<sup>b\*</sup>  
and Suchada Chantrapromma<sup>c\*</sup><sup>a</sup>Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China, <sup>b</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and <sup>c</sup>Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, ThailandCorrespondence e-mail: hkfun@usm.my,  
suchada.c@psu.ac.th

## Key indicators

Single-crystal X-ray study  
 $T = 297$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.051  
 $wR$  factor = 0.128  
Data-to-parameter ratio = 13.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

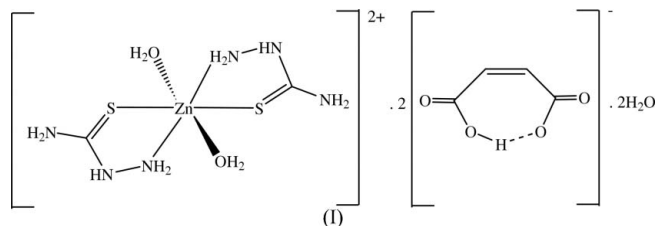
## Bis(thiosemicarbazide)zinc(II) bis(maleate) dihydrate

In the title compound,  $[\text{Zn}(\text{CH}_5\text{N}_3\text{S})_2(\text{H}_2\text{O})_2](\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , the  $\text{Zn}^{\text{II}}$  ion lies on a centre of symmetry and is coordinated by two pairs of N and S atoms from two symmetry-related thiosemicarbazide ligands and two O atoms from two water molecules in a distorted octahedral geometry. In the crystal structure, the components are effectively linked together by electrostatic interactions and hydrogen bonds of the  $\text{O}-\text{H} \cdots \text{O}$ ,  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{S}$  types into a three-dimensional network.

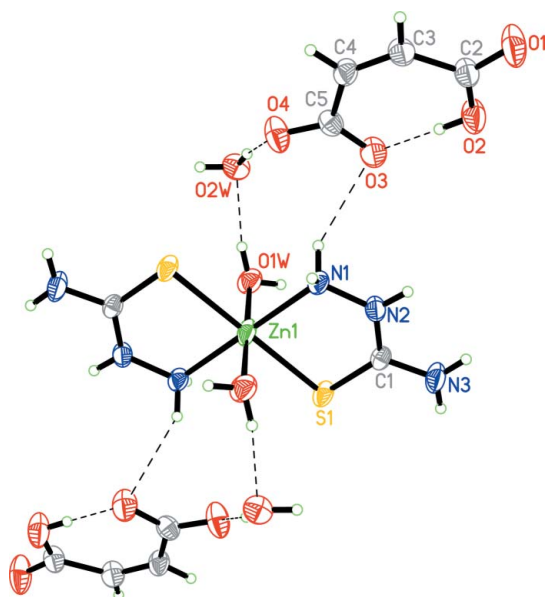
Received 4 November 2005  
Accepted 21 November 2005  
Online 26 November 2005

## Comment

The assembly of complexes on the basis of adding building units and connecting them is the most efficient means for the construction of highly organized structures. Transition-metal-directed self-assembly *via* coordination (Zhang, Li, Chen *et al.*, 2000; Philp & Stoddart, 1996) and crystal engineering based on the use of either coordinative bonds (Blake *et al.*, 1999) or weaker intermolecular interactions have attracted much interest. In the latter methodology, the hydrogen bond can influence the metal coordination geometry and adjust the structure of related compounds because of the relative strength, directionality, flexibility and dynamic character of the bond (Allen *et al.*, 1999; Russell *et al.*, 1997; Kawamoto *et al.*, 1996). Dicarboxylates are an important class of ligands in the formation of coordination polymers (Heinze *et al.*, 1998; Groeneman *et al.*, 1999), and the chemistry of metal complexes containing *S,N*-bidentate ligands has been studied widely because of the structural features and particular properties of these complexes (Fun *et al.*, 1996; West *et al.*, 1993). As part of our studies investigating the effective synthesis and the properties of complexes containing thiosemicarbazides and dicarboxylates, we report here the crystal structure of the title compound, (I).



The asymmetric unit of (I) contains one-half of a  $[\text{Zn}(\text{CH}_5\text{N}_3\text{S})_2(\text{H}_2\text{O})_2]^{2+}$  cation, with the other half being inversion-related by  $(-x, -y, 1 - z)$ , a dicarboxylate anion (maleate) and a water molecule (Fig. 1). The  $\text{Zn}^{\text{II}}$  atom lies on a centre of symmetry and is six-coordinated by N and S atoms from two symmetry-related bidentate thiosemicarbazide

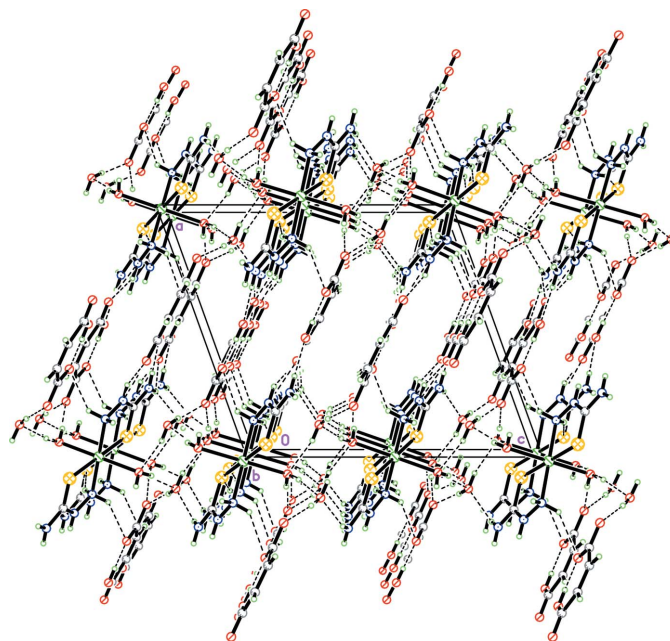

**Figure 1**

The components of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen bonds are shown as dashed lines. Unlabelled atoms are related to labelled atoms by the symmetry operation  $(-x, -y, 1 - z)$ .

ligands, and O atoms from two water molecules in a distorted octahedral geometry. The linear  $O1W-Zn1-O1W^i$  group [symmetry code: (i)  $-x, -y, 1 - z$ ] is nearly perpendicular to the equatorial  $N1/S1/N1^i/S1^i$  plane, as evidenced by the angles subtended at Zn1 (Table 1). The coordination bond lengths (Zn—O, Zn—N and Zn—S) are within normal ranges (Allen *et al.*, 1987), whereas the C1—S1 and C1—N2 bond distances are intermediate between the corresponding single- and double-bond lengths, suggesting electron delocalization in the thiosemicarbazide ligand upon complex formation. In contrast with related  $Zn^{II}$  compounds (Zhang, Li, Nishiura *et al.*, 2000; Burrows *et al.*, 2000), the maleate anion here does not coordinate to the  $Zn^{II}$  atom but acts as an independent counterion. This situation was also observed in the structures of *trans*-diaquabis(thiosemicarbazido-*k*<sup>2</sup>*N,S*)nickel(II) dimaleate dihydrate (Li, Usman, Razak, Fun *et al.*, 2003) and bis(thiosemicarbazido-*k*<sup>3</sup>*N,S*)nickel(II)-succinate-succinic acid (1/1/1) (Li, Usman, Razak, Rahman *et al.*, 2003).

The chelate ring  $N1/N2/C1/S1/Zn1$  is planar [r.m.s. deviation 0.016 Å], with the coordinated Zn1 atom displaced by 0.018 (1) Å. The maleate anion is also planar [r.m.s. deviation 0.027 Å], with deviations of 0.037 (2) and 0.043 (2) Å in opposite directions for atoms C4 and O4, respectively.

The complex cation, the maleate anions and the uncoordinated water molecules are linked by  $O2W-H2W2 \cdots O4$ ,  $O1W-H1W1 \cdots O2W$  and  $N1-H1N1 \cdots O3$  hydrogen bonds (Fig. 1), in which the maleate anions and the water molecules act as hydrogen-bond acceptors. The  $N1-H1N1 \cdots O3$ ,  $N1-H2N1 \cdots S1^i$ ,  $N2-H1N2 \cdots O1^{ii}$ ,  $N3-H1N3 \cdots O2^{ii}$  and  $N3-H2N3 \cdots O1^{iii}$  hydrogen bonds (see Table 2 for symmetry codes) link the complex cations and maleate anions into sheets parallel to the (102) plane (Fig. 2). The sheet consists of two


**Figure 2**

The crystal packing of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

different hydrogen-bonded ring patterns, *viz.*  $R_2^2(8)$  and  $R_3^2(9)$  (Bernstein *et al.*, 1995). An  $R_2^2(8)$  ring motif is generated by  $N-H \cdots O$  hydrogen bonds between a maleate anion and a symmetry-related thiosemicarbazide ligand, the  $R_3^2(9)$  ring motif is generated by  $N-H \cdots O$  hydrogen bonds linking a maleate anion to two symmetry-related thiosemicarbazide ligands, and another  $R_2^2(8)$  ring motif is generated by  $N-H \cdots S$  hydrogen bonds between two symmetry-related thiosemicarbazide ligands. The sheets are linked *via*  $O-H \cdots O$  and  $N-H \cdots O$  hydrogen bonds involving the water molecules, resulting in a three-dimensional network in the crystal structure.

## Experimental

Compound (I) was prepared by the self-assembly synthesis method. Zinc dichloride (0.299 g, 2.20 mmol), maleic acid (0.510 g, 4.40 mmol) and thiosemicarbazide (0.200 g, 2.20 mmol) were mixed together in a methanol/water (1:1 *v/v*) solution (50 ml) with stirring. The pH of the mixture was maintained at 4.8–5.0. The solution was then filtered and evaporated slowly at room temperature in air. Colourless single crystals of (I) suitable for X-ray analysis were obtained after 7 d.

### Crystal data

$[Zn(CH_5N_3S)_2(H_2O)_2] \cdot (C_4H_3O_4)_2 \cdot 2H_2O$   
 $M_r = 549.88$   
 Monoclinic,  $P2_1/c$   
 $a = 13.0748$  (2) Å  
 $b = 6.0256$  (1) Å  
 $c = 14.4306$  (1) Å  
 $\beta = 109.790$  (1)°  
 $V = 1069.75$  (3) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.707$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 6261 reflections  
 $\theta = 1.7$ – $26.0$ °  
 $\mu = 1.41$  mm<sup>-1</sup>  
 $T = 297$  (2) K  
 Block, colourless  
 $0.50 \times 0.28 \times 0.20$  mm

Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.628$ ,  $T_{\max} = 0.754$   
 6261 measured reflections

2096 independent reflections  
 1796 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.084$   
 $\theta_{\text{max}} = 26.0^\circ$   
 $h = -16 \rightarrow 14$   
 $k = -7 \rightarrow 7$   
 $l = -17 \rightarrow 15$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.128$   
 $S = 1.01$   
 2096 reflections  
 159 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.55 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.29 \text{ e } \text{Å}^{-3}$   
 Extinction correction: SHELXTL  
 Extinction coefficient: 0.019 (4)

Table 1

Selected geometric parameters (Å, °).

Zn1—N1	2.136 (2)	O4—C5	1.230 (4)
Zn1—O1W	2.344 (2)	N1—N2	1.410 (3)
Zn1—S1	2.3873 (6)	N2—C1	1.324 (3)
S1—C1	1.710 (3)	N3—C1	1.329 (3)
O1—C2	1.228 (4)	C2—C3	1.482 (4)
O2—C2	1.291 (3)	C3—C4	1.327 (4)
O3—C5	1.276 (3)	C4—C5	1.493 (4)
N1 <sup>i</sup> —Zn1—N1	180	O1W—Zn1—S1	90.63 (5)
N1 <sup>i</sup> —Zn1—O1W	85.35 (8)	N1—Zn1—S1 <sup>i</sup>	96.09 (5)
N1—Zn1—O1W	94.65 (8)	O1W—Zn1—S1 <sup>i</sup>	89.37 (5)
O1W—Zn1—O1W <sup>i</sup>	180	S1—Zn1—S1 <sup>i</sup>	180
N1—Zn1—S1	83.91 (5)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H1O2 <sup>i</sup> ··O3	0.82	1.61	2.429 (3)	179
N1—H1N1··O3	0.90	2.40	3.145 (3)	140
N1—H2N1··S1 <sup>ii</sup>	0.90	2.63	3.464 (2)	154
N2—H1N2··O1 <sup>iii</sup>	0.86	1.97	2.768 (3)	154
N3—H1N3··O2 <sup>iii</sup>	0.86	2.18	3.031 (4)	172
N3—H2N3··O1 <sup>iv</sup>	0.86	2.45	3.023 (3)	125
N3—H2N3··O2W <sup>v</sup>	0.86	2.33	3.097 (3)	149
O1W—H1W1··O2W	0.84 (4)	1.90 (4)	2.732 (3)	171 (4)
O1W—H2W1··O4 <sup>vi</sup>	0.84 (5)	1.96 (4)	2.789 (3)	169 (5)
O2W—H1W2··O1W <sup>vii</sup>	0.85 (3)	2.11 (3)	2.937 (3)	166 (3)
O2W—H2W2··O4	0.84 (3)	1.95 (3)	2.784 (3)	172 (3)

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

Water H atoms were located in a difference map and were refined with the restraints  $O-H = 0.84$  (1) Å and  $H \cdots H = 1.37$  (1) Å. All other H atoms were positioned geometrically and allowed to ride on

their parent atoms, with  $O-H = 0.82$  Å,  $N-H = 0.86-0.90$  Å and  $C-H = 0.93$  Å, and with  $U_{\text{iso}}(\text{H}) = 1.2-1.5U_{\text{eq}}(\text{carrier})$ . The deepest hole is located 0.92 Å from atom Zn1.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

This work was supported by the National Natural Science Foundation of China (grant Nos. 50272001, 50335050 and 50325311), the Education Office Foundation of Anhui Province (grant No. 2005 K J101), the Natural Science Foundation of Anhui Province (grant No. 03044701) and the Person Ability Foundation of Anhui Province (grant No. 2002Z021). YPT thanks the Ministry of Education of China. The authors also thank the Malaysian Government and Universiti Sains Malaysia for Scientific Advancement Grant Allocation (SAGA) grant No. 304/PFIZIK/635003/A118.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.  
 Allen, M. T., Burrows, A. D. & Mahon, M. F. (1999). *J. Chem. Soc. Dalton Trans.* pp. 215–222.  
 Bernstein, J., Davis, R. E., Simoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Blake, A. J., Champness, N. R., Hubberstey, P. Li, W. S., Withersby, M. A. & Schroder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.  
 Burrows, A. D., Harrington, R. W., Mahon, M. F. & Price, C. E. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3845–3854.  
 Fun, H.-K., Sivakumar, K., Tian, Y.-P., Duan, C.-Y., Lu, Z.-L. & You, X.-Z. (1996). *Acta Cryst.* **C52**, 1143–1145.  
 Groeneman, R. H., MacGillivray, L. R. & Atwood, J. L. (1999). *Inorg. Chem.* **38**, 208–209.  
 Heinze, K., Huttner, G. & Schober, P. (1998). *Eur. J. Inorg. Chem.* pp. 183–189.  
 Kawamoto, T., Hammes, B. S., Haggerty, B., Yap, G. P. A., Rheingold, A. L. & Borovik, A. S. (1996). *J. Am. Chem. Soc.* **118**, 285–286.  
 Li, S.-L., Usman, A., Razak, I. A., Fun, H.-K., Wu, J.-Y., Tian, Y.-P., Jiang, M.-H. & Chen, Z.-Y. (2003). *Acta Cryst.* **C59**, m181–m183.  
 Li, S.-L., Usman, A., Razak, I. A., Rahman, A. A., Fun, H.-K., Wu, J.-Y., Tian, Y.-P., Jiang, M.-H. & Chen, Z.-Y. (2003). *Acta Cryst.* **E59**, m199–m201.  
 Philp, D. & Stoddart, J. F. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1154–1196.  
 Russell, V. A., Evans, C. C., Li, W. & Ward, M. D. (1997). *Science*, **276**, 575–579.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.  
 West, D. X., Liberta, A. E., Padhye, S. B., Chicote, R. C., Sonawane, P. B., Kumbhar, A. S. & Yerrande, R. G. (1993). *Coord. Chem. Rev.* **123**, 49–71.  
 Zhang, Y., Li, J. M., Chen, J. H., Su, Q.-B., Deng, W., Nishiura, M., Imamoto, T., Wu, X. T. & Wang, Q. M. (2000). *Inorg. Chem.* **39**, 2330–2336.  
 Zhang, Y. G., Li, J. M., Nishiura, M., Hou, H.-Y., Deng, W. & Imamoto, T. (2000). *J. Chem. Soc. Dalton Trans.* pp. 293–297.