metal-organic papers

Sheng-Li Li,[a] Hoong-Kun Fun,[b]* Suchada Chantrapromma,[c]* Jie-Ying Wu[a] and Yu-Peng Tian[a]

[a]Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China, [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [c]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

Bis(thiosemicarbazide)cadmium(II) bis(maleate) dihydrate

In the title compound, $[Cd(CH_5N_3S)_2(H_2O)_2](C_4H_3O_4)_2\cdot 2H_2O$, the Cd^{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 O—H···O, N—H···O and N—H···S types into a three-dimensional network.

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. This is achieved due to the advancement of crystallography and synthetic chemistry (Abrahams *et al.*, 1999; Bowmaker *et al.*, 1998). Being the most efficient means for construction of highly organized structures and rational design of functional materials, transition-metal-directed self-assembly has emerged as a new and major motif-forming mechanism in supramolecular architecture. The study of self-assembly processes and properties of supramolecular systems and/or molecular aggregates in natural and non-natural systems (organic and inorganic systems) has attracted much interest (Lawrence *et al.*, 1995; Yaghi *et al.*, 1998). Meanwhile, there is considerable current interest in crystal engineering based on the use of either coordinative bonds (Blake *et al.*, 1999) or weaker intermolecular interactions. 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). As part of our studies investigating the synthesis and properties of complexes containing thiosemicarbazides, we report here the crystal structure of the title compound, (I), which is isomorphous with $[Zn(CH_5N_3S)_2(H_2O)_2]\cdot 2C_4H_3O_4\cdot 2H_2O$ (Li *et al.*, 2005).

(I)
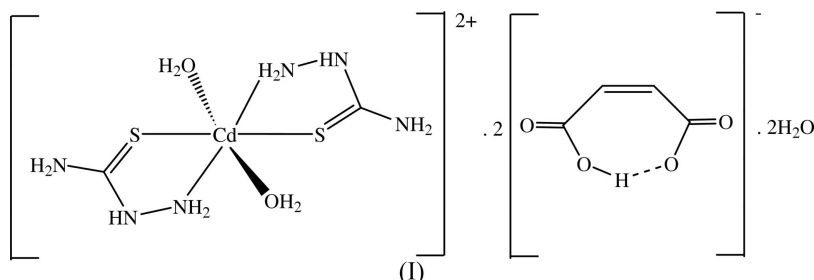
The asymmetric unit of (I) contains one-half of a $[Cd(CH_5N_3S)_2(H_2O)_2]^{2+}$ cation, the other half being inversion-related by $(-x, -y, 1 - z)$, a maleate anion and a water molecule (Fig. 1). The Cd^{II} atom lies on a centre of symmetry and is six-coordinated by two N, two S and two O atoms. Each of the two pairs of coordinated S and N atoms belongs to one of the two symmetry-related thiosemicarbazide ligands, in which the ligands serve as *N,S*-chelates, while the two coordinated O atoms belong to the symmetry-related water molecules. The CdN$_2$S$_2$O$_2$ group forms a slightly distorted octahedral configuration. The linear O1W—Cd1—O1W^i group [symmetry code: (i) $-x, -y, 1 - z$] is almost perpendicular to the equatorial N1/S1/N1^i/S1^i plane, as evidenced by the angles subtended at atom Cd1 (Table 1). The coordination bond lengths (Cd—O, Cd—N and Cd—S) are normal (Orpen *et al.*, 1989), whereas the C1—N2 and C1—S2 bond distances in the thiosemicarbazide ligands are intermediate between the corresponding single- and double-bond lengths. These C—N and C—S bonds suggest, to some extent, the electronic delocalization effect on the chelate ligand upon complex formation.

The structure differs from that of related compounds (Zhang, Li, Chen *et al.*, 2000; Zhang, Li, Nishiura *et al.*, 2000; Burrows *et al.*, 2000) in that the maleate group in (I) is not coordinated to the Cd^{II} atom but acts as an independent counter-ion, with mutual electrostatic interaction in the structure. This situation was also observed in our previous studies on the structures of *trans*-diaquabis(thiosemicarbazido-k^{2}N,S)nickel(II) dimaleate dihydrate (Li, Usman, Razak, Fun *et al.*, 2003), bis(thiosemicarbazido-k^{3}N,S) nickel(II)–succinate–succinic acid (1/1/1) (Li, Usman, Razak, Rahman *et al.*, 2003) and bis(thiosemicarbazide)zinc(II) bis(maleate) dihydrate (Li *et al.*, 2005).

The thiosemicarbazide ligand is planar (r.m.s. deviation 0.017 Å) and the coordinated Cd1 atom is displaced from it by 0.242 (3) Å. The maleate anion is also planar (r.m.s. deviation 0.028 Å), with deviations of 0.046 (2) and 0.043 (2) Å in opposite directions for atoms O1 and O2, respectively.

The complex cation, the maleate anions and the uncoordinated water molecules are linked by O1W—H1W1⋯O2W, O2W—H2W2⋯O4 and N1—H1N1⋯O3 hydrogen bonds (Fig. 1), in which the maleate anions and the water molecules act as hydrogen-bond acceptors. In the crystal packing, the thiosemicarbazide ligands, maleate anions and water molecules serve as both hydrogen-bond donors and acceptors. The N1—H2N1⋯S1^{ii}, N2—H1N2⋯O1^{iii}, N3—H1N3⋯O2^{iii} and N3—H2N3⋯O1^{iv} hydrogen bonds (see Table 2 for symmetry codes), together with the N1—H1N1⋯O3 hydrogen bond, link the complex cations and maleate anions into sheets parallel to the (10$\bar{2}$) plane (Fig. 2). The sheets are interconnected by N—H⋯O and O—H⋯O hydrogen bonds involving water molecules into a three-dimensional network.

Experimental

Compound (I) was prepared by the self-assembly synthesis method. Cadmium chloride (0.367 g, 2 mmol), maleic acid (0.464 g, 4 mmol)
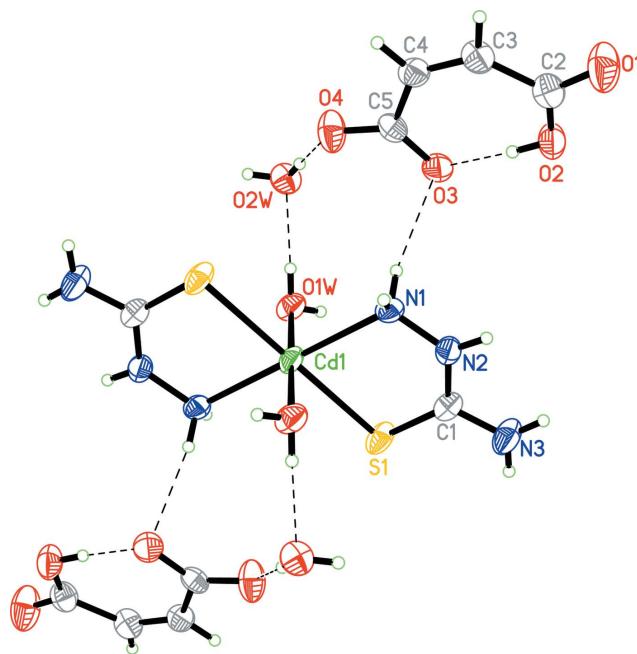

Figure 1
The components of (I), showing 80% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen bonds are shown as dashed lines. Unlabelled atoms are related to labelled atoms by the symmetry operation $(-x, -y, 1 - z)$.

and thiosemicarbazide (0.182 g, 2 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 from the reaction mother solution by the evaporation of the solvent after 7 d.

Crystal data

$[Cd(CH_5N_3S)_2(H_2O)_2]$-$(C_4H_3O_4)_2$·2H$_2$O	$D_x = 1.834$ Mg m^{-3}
$M_r = 596.90$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2471
$a = 12.4444$ (1) Å	reflections
$b = 6.1239$ (1) Å	$\theta = 1.7$–27.5°
$c = 14.9076$ (3) Å	$\mu = 1.27$ mm^{-1}
$\beta = 107.9569$ (10)°	$T = 297$ (2) K
$V = 1080.74$ (3) Å^3	Block, colourless
$Z = 2$	$0.40 \times 0.24 \times 0.22$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	2471 independent reflections
	2121 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.095$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$
	$h = -8 \rightarrow 16$
$T_{min} = 0.700$, $T_{max} = 0.756$	$k = -7 \rightarrow 7$
7169 measured reflections	$l = -19 \rightarrow 14$

Refinement

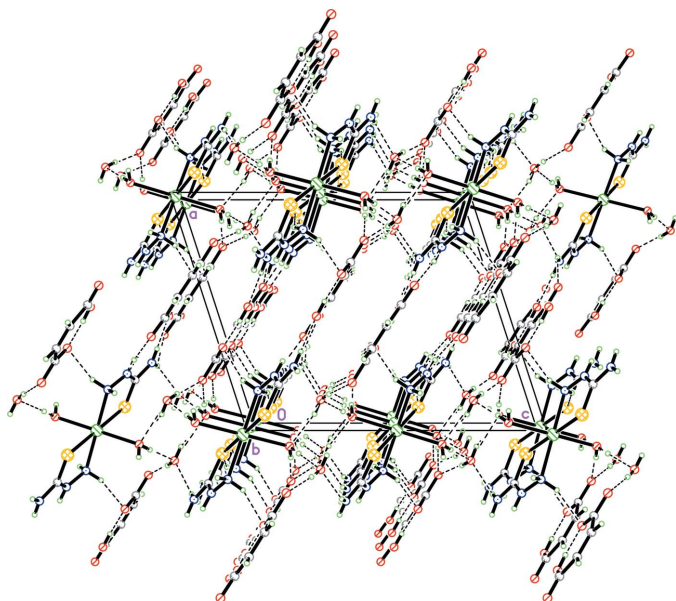|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 1.07$ e Å^{-3}
2471 reflections	$\Delta\rho_{min} = -2.68$ e Å^{-3}
159 parameters	Extinction correction: *SHELXTL*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0156 (16)

Figure 2
The crystal packing of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.352 (2)	O4—C5	1.239 (4)
Cd1—O1W	2.464 (2)	N1—N2	1.407 (3)
Cd1—S1	2.5433 (7)	N2—C1	1.334 (3)
S1—C1	1.715 (3)	N3—C1	1.331 (3)
O1—C2	1.232 (4)	C2—C3	1.496 (4)
O2—C2	1.298 (4)	C3—C4	1.325 (4)
O3—C5	1.287 (3)	C4—C5	1.496 (4)
N1—Cd1—N1^i	180	O1W—Cd1—S1	90.55 (6)
N1—Cd1—O1W	99.53 (8)	N1—Cd1—S1^i	101.70 (5)
N1^i—Cd1—O1W	80.47 (8)	O1W—Cd1—S1^i	89.45 (6)
O1W—Cd1—O1W^i	180	S1—Cd1—S1^i	180
N1—Cd1—S1	78.30 (5)		

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H1O2⋯O3	0.82	1.60	2.415 (3)	177
N1—H1N1⋯O3	0.90	2.20	3.020 (3)	152
N1—H2N1⋯S1^{ii}	0.90	2.60	3.420 (2)	152
N2—H1N2⋯O1^{iii}	0.86	1.95	2.772 (4)	160
N3—H1N3⋯O2^{iii}	0.86	2.20	3.056 (4)	171
N3—H2N3⋯O1^{iv}	0.86	2.40	3.009 (3)	128
N3—H2N3⋯O2W^v	0.86	2.33	3.068 (3)	144
O1W—H1W1⋯O2W	0.82 (5)	1.89 (5)	2.704 (3)	178 (6)
O1W—H2W1⋯O4^{vi}	0.79 (4)	1.98 (4)	2.761 (3)	172 (4)
O2W—H1W2⋯O1W^{vii}	0.80 (4)	2.09 (4)	2.871 (3)	166 (4)
O2W—H2W2⋯O4	0.80 (4)	1.96 (4)	2.757 (3)	175 (4)

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) $x, -y - \frac{1}{2}, z + \frac{1}{2}$; (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 isotropically. 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 or 0.90 Å and C—H = 0.93 Å, and with U_{iso}(H) = 1.2–1.5U_{eq}(carrier). The highest peak in the difference map is 1.07 Å from H2N3 and the deepest hole is 2.68 Å from atom Cd1.

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).

References

Abrahams, B. F., Batten, S. R., Grannas, M. J., Hamit, H., Hoskins, B. F. & Robson, R. (1999). *Angew. Chem. Int. Ed.* **38**, 1475–1477.
Allen, M. T., Burrows, A. D. & Mahon, M. F. (1999). *J. Chem. Soc. Dalton Trans.* pp. 215–222.
Blake, A. J., Champness, N. R., Hubberstey, P., Li, W. S., Withersby, M. A. & Schroder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.
Bowmaker, G. A., Kennedy, B. J. & Reid, J. C. (1998). *Inorg. Chem.* **37**, 3968–3974.
Burrows, A. D., Harrington, R. W., Mahon, M. F. & Price, C. E. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3845–3854.
Lawrence, D. S., Jiang, T. & Levett, M. (1995). *Chem. Rev.* **95**, 2229–2260.
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.* C**59**, 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.* E**59**, m199–m201.
Li, S.-L., Wu, J.-Y., Tian, Y.-P., Fun, H.-K. & Chantrapromma, S. (2005). *Acta Cryst.* E**61**, m2701–m2703.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989) *J. Chem. Soc. Dalton Trans.* pp. S1–83.
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.
Yaghi, O. M., Li, H., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.
Zhang, Y.-G., 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.