Acta Crystallographica Section C
**Crystal Structure
Communications**

ISSN 0108-2701

Dibenzyl 2,2′-(ethane-1,2-diylidene)dihydrazinecarbodithioate bis(dimethylformamide) solvate

Li Xu,† Jian-Hao Zhou, Xue-Tai Chen* and Xiao-Zeng You

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093, People's Republic of China
Correspondence e-mail: xtchen@netra.nju.edu.cn

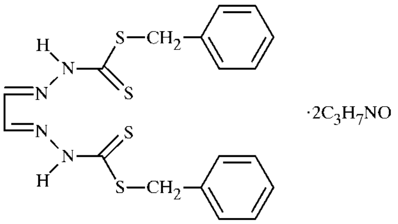
Received 3 August 2001
Accepted 27 June 2002
Online 31 July 2002

The title compound, $C_{18}H_{18}N_4S_4\cdot 2C_3H_7NO$, crystallizes with the dibenzyl dihydrazinecarbodithioate molecule residing on a crystallographic inversion centre. The molecule adopts a *trans* conformation with respect to the central C—C single bond. The dihedral angle between the phenyl group and the thiothiosemicarbazone unit is 74.1 (1)°.

Comment

Over the past three decades, metal complexes of *S*,*N*-chelating agents have been extensively studied because of their pronounced antibacterial, antiviral and anticancer biological activities (Ali & Livingstone, 1974). The majority of studies have focused on either *N*,*S*-bidentate or *N*,*N*,*S*-tridentate donor sequences in these ligands. The observation that the *S*,*N*,*N*,*S*-tetradentate ligand 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone) and its copper(II) chelate possess antineoplastic activities (Winkelmann *et al.*, 1974; Petering, 1974; Chan-Stier *et al.*, 1976; Minkel *et al.*, 1976, 1978; Minkel & Petering, 1978) provided an impetus for the study of tetradentate *S*,*N*-chelating ligands and transition-metal complexes of thiosemicarbazone. A number of nickel(II), copper(II) and zinc(II) chelates have been synthesized and characterized. Recently, the title compound, dibenzyl 2,2′-(ethane-1,2-diylidene)dihydrazinecarbodithioate bis(dimethylformamide) solvate, (I), and the corresponding nickel(II), copper(II), cadmium(II) and zinc(II) chelates, were reported to exhibit biological activity (Ali *et al.*, 1992). We obtained a single crystal of (I) and report herein its molecular and crystal structure.

The structure of (I), together with the atom-labelling scheme, is shown in Fig. 1. The two thiosemicarbazone moieties adopt a *trans* configuration with respect to the C9—C9^i bond, which minimizes the steric crowding in the molecule [symmetry code: (i) $-1 - x, 1 - y, 1 - z$]. No intramolecular hydrogen bonding is observed. The molecule sits on a crystallographic centre of symmetry, which resides at the midpoint of the C9—C9^i bond. There are three nearly planar groupings of atoms in the molecule, namely the two symmetry-related phenyl planes, with a mean deviation of 0.0025 Å, and the central plane consisting of atoms C7, S1, C8, S2, N1, N2, C9 and their symmetry equivalents, with a mean deviation of 0.0110 Å. The dihedral angle between the phenyl ring and the central plane is 74.1 (1)°.



(I)

Selected bond lengths and angles are listed in Table 1. The N2—C9 [1.275 (3) Å] and S2—C8 [1.647 (3) Å] bonds both exhibit double-bond character. The N1—C8 [1.337 (3) Å] and S1—C8 [1.746 (2) Å] bond distances are shorter than accepted covalent single-bond values (N—C 1.47 Å and C—S 1.81 Å; Xu, 1993; Lydon *et al.*, 1982), indicating their partial double-bond character, due to delocalization of the electrons in the S1—C8(═S2)—N1 π-system.

The bond angles around C8 illustrate the steric effect of the bulky benzyl substituent, with the result that the S1—C8—S2 angle is 125.44 (15)°, compared with a value of 112.77 (18)° for N1—C8—S1 and 121.78 (18)° for N1—C8—S2. There are weak intermolecular C9—H9*A*···O1 and N1—H1*A*···O1 hydrogen bonds between the dibenzyl dihydrazinecarbodithioate molecule and the dimethylformamide solvent molecules (details are given in Table 2). There are no other significant interactions, such as π–π stacking, found in the crystal structure.

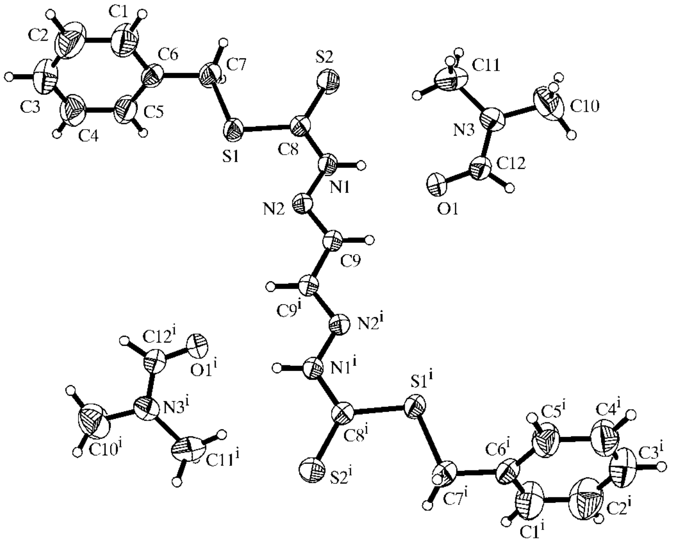


Figure 1
A view of the structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-1 - x, 1 - y, 1 - z$.]

---

† Alternative address: Information College of Science and Technology, Nanjing Forestry University, Nanjing 210037, People's Republic of China.

DOI: 10.1107/S0108270102011411

Experimental

The title compound was prepared by refluxing *S*-benzyldithiocarbazate and a 30% aqueous solution of glyoxal (molar ratio 2:1) in absolute ethanol for *ca* 5 min (Ali *et al.*, 1992). Diffraction-quality crystals of (I) were obtained by recrystallization from dimethylformamide.

Crystal data

$C_{18}H_{18}N_4S_4 \cdot 2C_3H_7NO$
$M_r = 564.84$
Triclinic, $P\overline{1}$
$a = 6.1040\ (10)$ Å
$b = 10.3202\ (18)$ Å
$c = 11.960\ (2)$ Å
$\alpha = 94.863\ (3)^\circ$
$\beta = 94.078\ (3)^\circ$
$\gamma = 99.867\ (3)^\circ$
$V = 736.8\ (2)$ Å^3

$Z = 1$
$D_x = 1.273$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1445 reflections
$\theta = 2.8$–25.9°
$\mu = 0.35$ mm^{-1}
$T = 293\ (2)$ K
Prism, pale yellow
$0.25 \times 0.22 \times 0.17$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.913$, $T_{\max} = 0.942$
4486 measured reflections

3156 independent reflections
1900 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\max} = 27.9^\circ$
$h = -7 \rightarrow 8$
$k = -13 \rightarrow 11$
$l = -15 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.130$
$S = 1.00$
3156 reflections
168 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.063P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C7	1.818 (3)	N2—C9	1.275 (3)
S1—C8	1.746 (2)	N3—C10	1.442 (4)
S2—C8	1.647 (3)	N3—C11	1.439 (4)
N1—C8	1.337 (3)	N3—C12	1.317 (4)
N1—N2	1.367 (3)	O1—C12	1.211 (3)
C7—S1—C8	101.86 (12)	S1—C7—C6	106.70 (19)
N2—N1—C8	120.34 (19)	S1—C8—S2	125.44 (15)
N1—N2—C9	115.60 (19)	N1—C8—S1	112.77 (18)
C10—N3—C11	119.1 (3)	N1—C8—S2	121.78 (18)
C10—N3—C12	120.8 (3)	N2—C9—C9$^{\rm i}$	118.5 (3)
C11—N3—C12	119.8 (3)	N3—C12—O1	127.3 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O1	0.93	2.36	3.147 (3)	143
N1—H1*A*···O1	0.86	2.01	2.833 (2)	160

Atom H12 (bonded to C12) was located from a difference map. The remaining H atoms were placed geometrically and refined using a riding model, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.86 Å.

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*.

This work was supported by a Natural Science Grant from Jiangsu Province (BK99032).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1039). Services for accessing these data are described at the back of the journal.

References

Ali, M. A., Haroon, C. M., Nazimuddin, M., Majumder, S. M. M., Tarafder, M. T. H. & Khair, M. A. (1992). *Transition Met. Chem.* **17**, 133–136.
Ali, M. A. & Livingstone, S. E. (1974). *Coord. Chem. Rev.* **13**, 101–132, and references therein.
Chan-Stier, C. H., Minkel, D. T. & Petering, D. H. (1976). *Bioinorg. Chem.* **6**, 203–217.
Lydon, J. D., Elder, R. C. & Deutsch, E. (1982). *Inorg. Chem.* **21**, 3186–3197.
Minkel, D. T., Chan-Stier, C. H. & Petering, D. H. (1976). *Mol. Pharmacol.* **12**, 1036–1044.
Minkel, D. T. & Petering, D. H. (1978). *Cancer Res.* **38**, 117–123.
Minkel, D. T., Saryan, A. L. & Petering, D. H. (1978). *Cancer Res.* **38**, 124–129.
Petering, D. H. (1974). *Biochem. Pharmacol.* **23**, 567–576.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Winkelmann, D. A., Bermke, Y. & Petering, D. H. (1974). *Bioinorg. Chem.* **3**, 261–277.
Xu, S. (1993). *Organic Chemistry*, 2nd ed., p. 6. Beijing: High Educational Press.