

***mer*-Bis(1,4-dibenzoylthiosemicarbazidato- κ^3 O,N,O')cobalt(II)**

Yuan-Zhen Ke, Leng-Feng Zheng, Jian-Hai Luo, Xi-He Huang* and Chang-Cang Huang

Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: xhhuang@fzu.edu.cn

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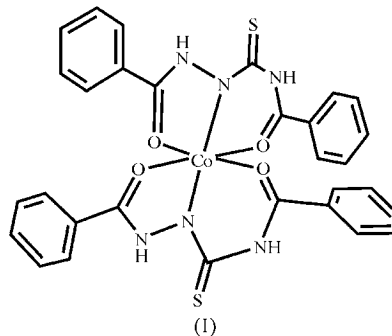
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The title complex, $[\text{Co}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}_2\text{S})_2]$, consists of an octahedrally coordinated Co^{II} ion, with two crystallographically independent 1,4-dibenzoylthiosemicarbazidate ligands in a tridentate *mer* coordination [$\text{Co}-\text{O} = 2.064(3)$ – $2.132(3)$ Å and $\text{Co}-\text{N} = 2.037(3)$ – $2.043(3)$ Å]. There are intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds involving one ligand and strong $\pi-\pi$ stacking interactions involving the other ligand, resulting in a three-dimensional supramolecular framework. The hydrogen bonds and $\pi-\pi$ interactions, as well as different intramolecular aryl-benzamide $\text{H}-\text{C}\cdots\text{H}(-\text{N})$ distances, give rise to a difference in conformation between the two ligands.

Comment

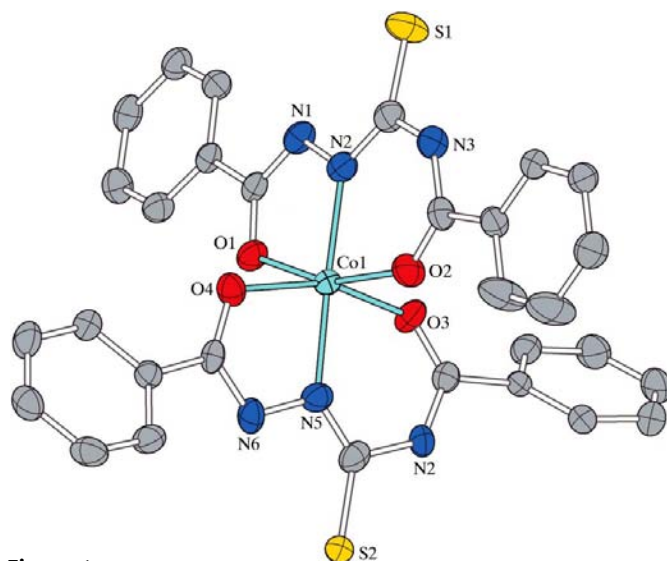
Thiosemicarbazones and their metal complexes are of great pharmacological interest owing to their various biological activities, including antibacterial, antimalarial, antiviral and antitumor (Quiroga & Ranninger, 2004; Kasuga *et al.*, 2003; Easmon *et al.*, 2001). These activities are greatly affected by the electronics, redox properties, number and position of substituent groups attached to the ligands, and the backbone conformation of the ligands or their metal complexes (Dearling *et al.*, 2002; Maurer *et al.*, 2002; Fettrai *et al.*, 2000). Supramolecular interactions might also play an important role in their biological activities. Intermolecular interactions, especially pairs of $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, often give rise to distortions of the conformation of the ligand backbone. Furthermore, these intermolecular interactions might allow the complexes to interact with various biological molecules containing complementary hydrogen-bonding motifs (*e.g.* purines, pyrimidines and peptide bonds) (Blower *et al.*, 2003). Therefore, it is of interest to obtain a deeper insight into the structure–function relationship, particularly for structures containing supramolecular interactions, such as hydrogen bonding, $\pi-\pi$ stacking, $\text{C}-\text{H}\cdots\pi$ and electrostatic interactions.

Hitherto, a large number of thiosemicarbazone ligands have been synthesized and structurally characterized; however, only a few 1,4-bisacylthiosemicarbazone ligands have been reported (Yamin & Yusof, 2003; Yusof *et al.*, 2003; Ali *et al.*, 2004). In the present study, the structure of the title cobalt complex, (I), with 1,4-dibenzoylthiosemicarbazidate (bhctb) has been determined; this represents the first example of a transition metal complex of such ligands.



Complex (I) contains a Co^{II} ion and two crystallographically independent bhctb ligands. The Co^{II} ion is in a slightly distorted octahedral coordination of two bhctb ligands (Fig. 1 and Table 1). Both of the tridentate bhctb ligands adopt a *mer*-coordination mode with the Co^{II} center through one N atom and two carbonyl O atoms, $\text{Co}(\text{ONO})(\text{ONO})$, forming one five-membered and one six-membered chelate ring. Owing to the spatial restrictions of the bhctb ligands, the bond angles in the Co coordination environment deviate from 90° and 180° by as much as $15.96(11)$ and $20.34(11)^\circ$, respectively.

Interestingly, there is a distinct difference between the conformations of the two crystallographically independent bhctb ligands. One bhctb ligand (containing atoms N1–N3 and denoted L1) exhibits greater coplanar characteristics, with a dihedral angle of $10.38(25)^\circ$ between the two phenyl groups, whereas the other bhctb ligand (containing N4–N6 and

**Figure 1**

A view of (I), with displacement ellipsoids shown at the 30% probability level. H atoms have been omitted for clarity and only Co, O, N and S atoms are labeled.

denoted *L2*) is contorted, with a larger dihedral angle [28.03 (11)°]. This significant difference is ascribed to intramolecular H···H repulsion, intermolecular hydrogen bonds and π - π interactions. The aryl-benzamide H-C···H(-N) distances in *L2* [H6A···H26 = 2.18 (3) Å and H4A···H20 = 2.294 (15) Å] are notably longer than those in *L1* [H1A···H1 = 2.01 (2) Å and H3A···H11 = 1.998 (17) Å], implying a lower repulsion in *L2*. There are two N-H···S hydrogen bonds [N···S = 3.505 (3) Å], related by a twofold axis, binding the two *L2* ligands into a dimer (Fig. 2 and Table 2). The presence of N-H···S hydrogen bonds and the lower H···H repulsion contribute to the conformational stabilization of *L2*. Furthermore, there are strong π - π stacking interactions between the *L1* ligands, which are consistent with the greater coplanarity of the rings in *L1*. Each *L1* ligand interacts with three adjacent *L1* ligands at distances between 3.158 (5) and 3.379 (7) Å, resulting in a three-dimensional supramolecular framework (Fig. 3).

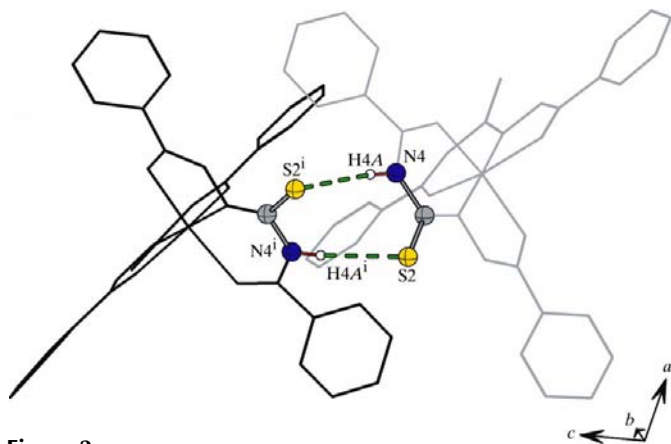


Figure 2
A pair of N-H···S hydrogen bonds binding two *L2* bhctb molecules into a dimer. Hydrogen bonds are denoted by dashed lines. Most of the H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$]

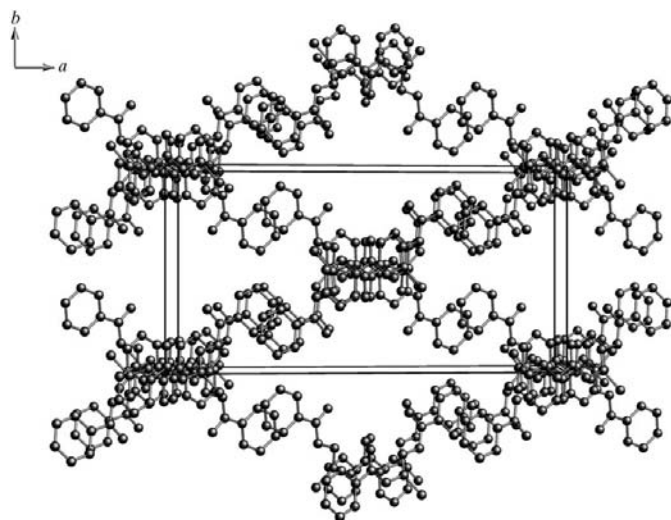


Figure 3
A view of the three-dimensional supramolecular framework formed from π - π stacking interactions involving *L1* ligands. The Co atoms and *L2* ligands have been omitted for clarity.

Experimental

1,4-Dibenzoylthiosemicarbazide (0.0293 g, 0.1 mmol) and cobalt(II) chloride hexahydrate (0.0476 g, 0.2 mmol) were dissolved in a mixed solvent of methanol and chloroform (12 ml, 2:1 v/v). Et₃N (0.014 ml) was then added and the solution stirred for 2 h at room temperature. The resulting red mixture was filtered and the filtrate was allowed to evaporate in air at room temperature. Red rod-shaped crystals were separated from the filtrate after seven days.

Crystal data

| | |
|---|---|
| [Co(C ₁₅ H ₁₂ N ₃ O ₂ S) ₂] | $V = 5774 (2) \text{ \AA}^3$ |
| $M_r = 655.62$ | $Z = 8$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a = 24.493 (5) \text{ \AA}$ | $\mu = 0.79 \text{ mm}^{-1}$ |
| $b = 12.355 (3) \text{ \AA}$ | $T = 298 (2) \text{ K}$ |
| $c = 19.539 (4) \text{ \AA}$ | $0.32 \times 0.28 \times 0.24 \text{ mm}$ |
| $\beta = 102.43 (3)^\circ$ | |

Data collection

| | |
|------------------------------------|--|
| Rigaku R-Axis RAPID diffractometer | 6613 independent reflections |
| 25840 measured reflections | 3364 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.095$ |

Refinement

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.055$ | 388 parameters |
| $wR(F^2) = 0.119$ | H-atom parameters constrained |
| $S = 1.01$ | $\Delta\rho_{max} = 0.51 \text{ e \AA}^{-3}$ |
| 6613 reflections | $\Delta\rho_{min} = -0.31 \text{ e \AA}^{-3}$ |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-------------|-----------|-------------|
| Co1—N5 | 2.037 (3) | Co1—O1 | 2.100 (2) |
| Co1—N2 | 2.043 (3) | Co1—O3 | 2.102 (3) |
| Co1—O2 | 2.064 (3) | Co1—O4 | 2.132 (3) |
| N5—Co1—N2 | 176.46 (12) | N5—Co1—O4 | 77.47 (13) |
| N5—Co1—O1 | 105.96 (11) | N2—Co1—O4 | 102.52 (12) |
| N2—Co1—O1 | 77.57 (11) | O3—Co1—O4 | 159.66 (11) |
| O2—Co1—O1 | 160.80 (10) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------|-------|-------------|-------------|---------------|
| N4—H4A···S2 ⁱ | 0.86 | 2.65 | 3.505 (3) | 172 |

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

H atoms attached to C and N atoms were positioned geometrically and refined using a riding model [C—H = 0.93 Å, N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$].

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3082). Services for accessing these data are described at the back of the journal.

References

- Ali, H., Yusof, M. S., Khamis, N. A., Mardi, A. S. & Yamin, B. M. (2004). *Acta Cryst.* **E60**, o1656–o1658.
- Blower, P. J., Castle, T. C., Cowley, A. R., Dilworth, J. R., Donnelly, P. S., Labisbal, E., Sowrey, F. E., Teat, S. J. & Went, M. J. (2003). *Dalton Trans.* pp. 4416–4425.
- Dearling, J. L. J., Lewis, J. S., Mullen, G. E. D., Welch, M. J. & Blower, P. J. (2002). *J. Biol. Inorg. Chem.* **7**, 249–259.
- Easmon, J., Puerstinger, G., Heinisch, G., Roth, T., Fiebig, H. H., Heinz, H., Holzer, W., Jaegar, W., Jenny, M. & Hofmann, J. (2001). *J. Med. Chem.* **44**, 2164–2171.
- Fettrai, M. B., Capacchi, S., Reffo, G., Pelosi, G., Tarasconi, P., Albertini, R., Pinelli, S. & Lunghi, P. (2000). *J. Inorg. Biochem.* **81**, 89–97.
- Kasuga, N. C., Sekino, K., Ishikawa, M., Honda, A., Yokoyama, M., Nakano, S., Shimada, N., Koumo, C. & Nomiya, K. (2003). *J. Inorg. Biochem.* **96**, 298–310.
- Maurer, R. I., Blower, P. J., Dilworth, J. R., Reynolds, C. A., Zheng, Y. F. & Mullen, G. E. D. (2002). *J. Med. Chem.* **45**, 1420–1431.
- Quiroga, A. G. & Ranninger, C. N. (2004). *Coord. Chem. Rev.* **248**, 119–133.
- Rigaku (1998). *RAPID-AUTO*. PC Version. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1993). *SHELXTL/PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Yamin, B. M. & Yusof, M. S. M. (2003). *Acta Cryst.* **E59**, o124–o126.
- Yusof, M. S. M., Yamin, B. M. & Shamsuddin, M. (2003). *Acta Cryst.* **E59**, o810–o811.