

Poly[bis(μ -4-benzoyl-1-isonicotinoylthiosemicarbazide- κ^2 N:S)dichlorido-cadmium(II)]

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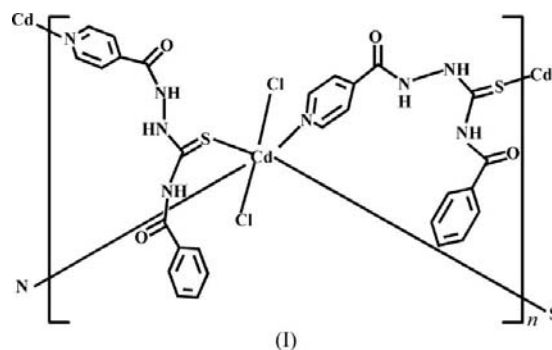
The asymmetric unit of the title complex, $[\text{CdCl}_2(\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2\text{S})_2]_n$, consists of one Cd^{II} ion located on the crystallographic inversion centre, one 4-benzoyl-1-isonicotinoylthiosemicarbazide ligand and one chloride ligand. The central Cd^{II} ion adopts a distorted octahedral coordination geometry formed by two pyridyl N atoms of two ligands, two S atoms of two other ligands and two chloride ligands. The thiosemicarbazide ligands act as bridges, linking the metal ions into a two-dimensional layered structure parallel to the bc plane. Intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and $\text{C}-\text{H}\cdots\pi$ interactions exist between adjacent layers.

Comment

Thiosemicarbazides and their derivatives have attracted considerable interest, not only because of their potentially beneficial biological properties, such as antibacterial, anti-tumour and antiviral activities (Angelusiu *et al.*, 2009; Belicchi-Ferrari *et al.*, 2007; Palaska *et al.*, 2002), but also because of their flexibility, which allows the ligands to bend and rotate freely to accommodate the coordination geometries of various metal centres. Many metal complexes derived from thiosemicarbazone, particularly the 1,4-disubstituted derivatives, have been prepared and characterized, and have been found to possess a wide variety of biological activities (Floquet *et al.*, 2009; Leovac *et al.*, 2009; Hassanien *et al.*, 2008; Latheef *et al.*, 2006; Babb *et al.*, 2003; Simonov *et al.*, 2002; Belicchi-Ferrari *et al.*, 2000). However, only a few 1,4-diacylthiosemicarbazone ligands have been reported so far (Xue *et al.*, 2006; Ali *et al.*, 2004; Yamin & Yusof, 2003; Yusof *et al.*, 2003). Acylthiosemicarbazide ligands contain O, S and N as potential donor atoms and can support mononuclear, multinuclear or even extended structure complexes. They can also form hydrogen bonds in the crystal structure, which is very

important in the design and synthesis of novel supramolecular structures.

Recently, much attention has been paid to coordination polymers with a framework structure, because of their potential applications and theoretical significance (Uemura *et al.*, 2009; Tranchemontagne *et al.*, 2009; Kurmoo, 2009; Lee *et al.*, 2009; Batten & Robson, 1998). However, there is no previous report of coordination polymers with a 1,4-diacylthiosemicarbazide ligand. Our group reported the first transition metal complex with a 1,4-diacylthiosemicarbazide ligand (Ke *et al.*, 2007), and that cobalt complex is mononuclear. In order to connect the metal centres to form a framework, we increased the possible donor atoms by replacing one of the phenyl groups with a pyridine ring. We report here the title two-dimensional coordination polymer, (I), which is the first transition metal complex with such ligands with an extended structure.



The asymmetric unit of complex (I) contains one Cd^{II} ion located on an inversion centre, one independent thiosemicarbazide ligand and one chloride ligand. The local coordination geometry around the Cd^{II} centre can be described as distorted octahedral (Fig. 1 and Table 1). The equatorial plane is formed by two pyridyl N atoms from two thiosemicarbazide ligands and two chloride ligands, while the axial positions are occupied by two S atoms from two other thiosemicarbazide ligands.

Each thiosemicarbazide ligand acts as a linear linker to coordinate two metal centers, while each metal ion is linked by four ligands and two chloride ligands in a *trans* configuration. Thus, two-dimensional undulating layers are formed parallel

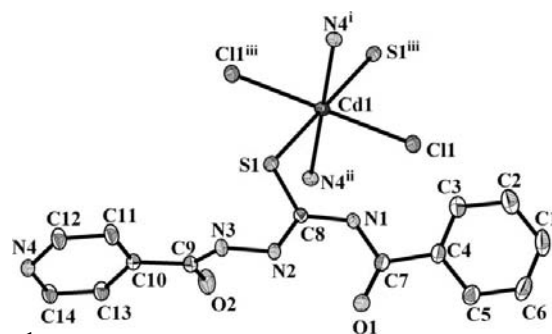


Figure 1

The structure of (I), showing the atom-labelling scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, y - 1, -z + \frac{3}{2}$; (ii) $x, -y + 2, z - \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$.]

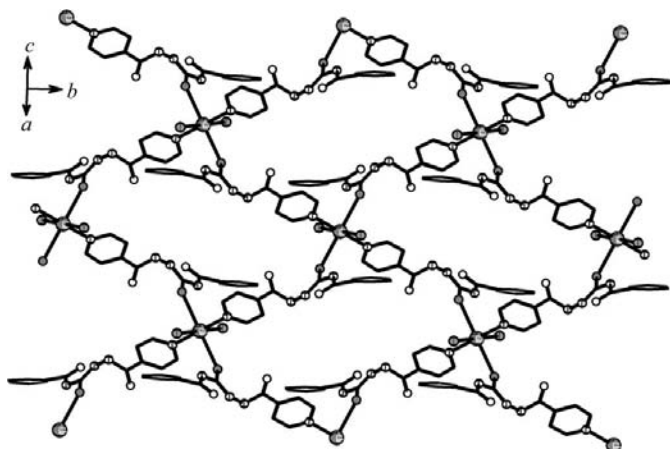


Figure 2
A view of the two-dimensional layer in (I). All H atoms have been omitted and all C atoms are shown as wires or sticks for clarity.

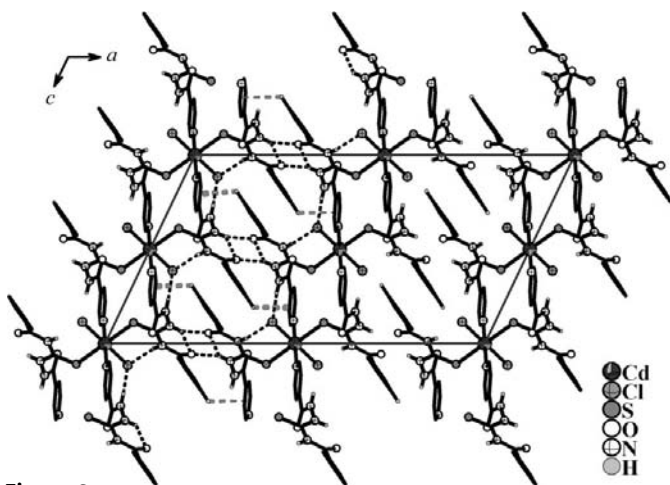


Figure 3
A packing diagram for (I), showing some of the hydrogen bonds (dark dashed lines) and C—H... π interactions (gray dashed lines). Most of the H atoms have been omitted except for those involved in the weak interactions. All C atoms are shown as wires or sticks.

to the *bc* plane (Fig. 2). The benzoyl groups are located on both sides of the layers. There are three types of intralayer hydrogen bonds, namely N1—H1...Cl1, N3—H3...Cl1 and N2—H10...O1, while there is one type of interlayer hydrogen bond. Neighboring layers are further connected to each other via N2—H10...O1 hydrogen bonds [N2...O1 = 3.010 (3) Å and N2—H10...O1 = 141°] and C6—H6... π interactions [C6...pyridyl = 3.327 (4) Å and C6—H6...Cg = 122°] (Fig. 3 and Table 2).

Compared with the previously reported cobalt complex (Ke *et al.*, 2007), in this cadmium polymer the ligands coordinate to the Cd^{II} ions via atoms N4 and S1 in a bridging motif, and the structure is characterized by a two-dimensional architecture. The dihedral angle between the phenyl and pyridyl groups is 39.46 (9)°. However, in the previously reported complex, the tridentate ligands coordinate to the Co^{II} centre through one N atom and two carbonyl O atoms in a chelating mode and the complex presents a mononuclear structure. The dihedral angles between the two phenyl groups are 28.03 (1) and

10.38 (2)°. The difference indicates that 1,4-diacylthiosemicarbazone ligands have varied coordination motifs.

Experimental

The thiosemicarbazide ligand was prepared according to Xue *et al.* (2006). The ligand (0.0189 g, 0.10 mmol) and cadmium chloride hydrate (0.0115 g, 0.05 mmol) were dissolved in a mixed solvent of methanol and *N,N*-dimethylformamide (11 ml, 10:1 *v/v*). After 5 min, dichloromethane (2 ml) was added and the solution was stirred for 3 h at room temperature. Colourless cube-shaped crystals of (I) crystallized from the solvent mixture after about 10 d.

Crystal data

[CdCl ₂ (C ₁₄ H ₁₂ N ₄ O ₂ S) ₂]	<i>V</i> = 3043.5 (11) Å ³
<i>M_r</i> = 783.97	<i>Z</i> = 4
Monoclinic, <i>C2/c</i>	Mo <i>K</i> α radiation
<i>a</i> = 26.272 (5) Å	μ = 1.08 mm ⁻¹
<i>b</i> = 8.8773 (18) Å	<i>T</i> = 293 K
<i>c</i> = 14.453 (3) Å	0.24 × 0.21 × 0.17 mm
β = 115.46 (3)°	

Data collection

Rigaku Mercury CCD area-detector diffractometer	3494 independent reflections
12400 measured reflections	3349 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.035

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.037	205 parameters
<i>wR</i> (<i>F</i> ²) = 0.068	H-atom parameters constrained
<i>S</i> = 1.23	$\Delta\rho_{\max}$ = 0.39 e Å ⁻³
3494 reflections	$\Delta\rho_{\min}$ = -0.26 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Cd1—N4 ⁱ	2.373 (2)	Cd1—S1	2.7364 (8)
Cd1—Cl1	2.5828 (10)		
N4 ⁱ —Cd1—Cl1	90.76 (6)	Cl1—Cd1—S1	96.09 (2)
N4 ⁱ —Cd1—S1	90.77 (6)		

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

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the N4/C10—C14 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...Cl1	0.86	2.39	3.214 (2)	161
N3—H3...Cl1 ⁱⁱ	0.86	2.48	3.283 (3)	156
N2—H10...O1	0.86	1.98	2.637 (3)	132
N2—H10...O1 ⁱⁱⁱ	0.86	2.30	3.010 (3)	141
C6—H6...Cg1 ⁱⁱⁱ	0.93	2.74	3.327 (4)	122

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

All H atoms bonded to C and N atoms were allowed for in idealized positions using the riding-model approximation, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C), and N—H = 0.86 Å and *U*_{iso}(H) = 1.2*U*_{eq}(N).

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve

structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3054). Services for accessing these data are described at the back of the journal.

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