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Crystal structure of bis(*N'*-((5-(ethoxycarbonyl)-1*H*-pyrrol-2-yl)methylene)-*N*-ethylcarbamohydrazonothioato- κ^2 N,O)nickel(II), $C_{22}H_{30}N_8O_4S_2Ni$

Table 1: Data collection and handling.

Crystal:	Black block
Size:	0.18 × 0.15 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.93 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6691, 2353, 0.045
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1692
$N(\text{param})_{\text{refined}}$:	171
Programs:	SHELX [1], Bruker [2]

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Abstract

$C_{22}H_{30}N_8O_4S_2Ni$, monoclinic, $P2_1/c$ (no. 14), $a = 10.635(2)$ Å, $b = 10.308(2)$ Å, $c = 12.444(3)$ Å, $\beta = 101.205(4)^\circ$, $V = 1338.2(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0417$, $wR_{\text{ref}}(F^2) = 0.0937$, $T = 296(2)$ K.

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The molecular structure is shown in the figure (hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title complex was synthesized by the reaction of *N'*-((*Z*)-(5-(ethoxycarbonyl)-1*H*-pyrrol-2-yl)methylene)-*N*-ethylcarbamohydrazonothioic acid (TSCH) (5 mmol) with an equimolar amount of $Ni(OAc)_2 \cdot 6H_2O$ in MeOH/THF (20 mL,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.44432(8)	0.68589(9)	0.42404(8)	0.0493(3)
Ni1	0.5000	0.5000	0.5000	0.03433(19)
O1	−0.1130(2)	0.6728(2)	0.6376(2)	0.0515(6)
O2	−0.1857(2)	0.5482(2)	0.7619(2)	0.0557(7)
N1	0.1064(2)	0.5305(2)	0.6593(2)	0.0381(7)
H1	0.0966	0.5843	0.6055	0.046*
N2	0.3471(2)	0.5143(2)	0.5600(2)	0.0346(6)
N3	0.2515(2)	0.6034(2)	0.5176(2)	0.0368(6)
N4	0.2110(2)	0.7809(3)	0.4063(2)	0.0450(7)
H4	0.2388	0.8351	0.3638	0.054*
C1	−0.2329(4)	0.8346(4)	0.5256(3)	0.0655(11)
H1A	−0.2354	0.7818	0.4616	0.098*
H1B	−0.1573	0.8876	0.5370	0.098*
H1C	−0.3075	0.8890	0.5155	0.098*
C2	−0.2305(3)	0.7496(4)	0.6227(3)	0.0582(10)
H2A	−0.2318	0.8018	0.6873	0.070*
H2B	−0.3048	0.6930	0.6109	0.070*
C3	−0.1030(3)	0.5770(3)	0.7113(3)	0.0458(9)
C4	0.0195(3)	0.5101(3)	0.7256(3)	0.0419(8)
C5	0.0703(3)	0.4174(3)	0.8012(3)	0.0518(10)
H5	0.0320	0.3845	0.8566	0.062*
C6	0.1887(3)	0.3820(3)	0.7801(3)	0.0486(9)
H6	0.2440	0.3210	0.8190	0.058*
C7	0.2104(3)	0.4529(3)	0.6911(3)	0.0376(8)
C8	0.3206(3)	0.4472(3)	0.6414(3)	0.0370(8)
H8	0.3823	0.3866	0.6715	0.044*
C9	0.2907(3)	0.6877(3)	0.4521(3)	0.0355(8)
C10	0.0806(3)	0.7973(3)	0.4230(3)	0.0455(9)
H10A	0.0817	0.8328	0.4954	0.055*

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H10B	0.0378	0.7138	0.4183	0.055*
C11	0.0085(3)	0.8879(4)	0.3370(3)	0.0617(11)
H11A	0.0021	0.8494	0.2658	0.093*
H11B	0.0536	0.9688	0.3393	0.093*
H11C	−0.0759	0.9029	0.3511	0.093*

v:*v* = 1:1). The reaction mixture was filtered and set aside to crystallize for several days, giving black block crystals.

Experimental details

The structure was solved by direct methods and refined with the SHELX crystallographic software package [1]. The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Comment

Thiosemicarbazones (TSCs) and their transition metal complexes have attracted attention in the coordination chemistry because of their high biological and pharmaceutical activities, such as antibacterial, antiviral, antifungal, antitumor activity and so on [3, 4]. It is noted that *N*(4)-substituted TSCs bearing pyrrole units could act as potential chemotherapeutic agents [5, 6]. Herein, the title Ni(II) complex with a pyrrole-TSC ligand is reported, which was synthesized and characterized by X-ray diffraction.

In the title structure, the asymmetric unit contains one half of the complex with Ni1 atom lying on the inversion center [the figure, symmetry code: (i) $-x + 1, -y + 1, -z + 1$]. The four-coordinated Ni(II) ion is in a distorted square planar geometry with the donor sets of two N and two S atoms from two dependent TSC ligands. The length of C–S is 1.736(3) Å, which is much longer than that of 1.691(19) Å in the free molecule [6], showing that the TSC ligand has thiolated and deprotonated. Furthermore, the imine C=N (C8–N2) bond

adopted a *Z* configuration instead of *E* in the free molecule [6]. In the solid state, intermolecular N–H···O hydrogen bonds between the terminal amino N and carboxylate O atoms link molecules into a two-dimensional supermolecular network. In addition, the intramolecular N–H···N hydrogen bond between the pyrrole N and the imine N (N3) atom is present (see the Figure). All egmetic parameters are similar to those derived for the parent structure [7] and related ones [8].

References

- Sheldrick, G. M.: Crystal refinement with SHELX. *Acta Crystallogr.* **C71** (2015) 3–8.
- Bruker. SMART and SAINT. Bruker AXS Inc., Madison, WI, USA (2007).
- Palanimuthu, D.; Shinde, S. V.; Somasundaram, K.; Samuelson, A. G.: *In vitro* and *in vivo* anticancer activity of copper bis(thiosemicarbazone) complexes. *J. Med. Chem.* **56** (2013) 722–734.
- Matesanz, A. I.; Leitao, I.; Souza, P.: Palladium(II) and platinum(II) bis(thiosemicarbazone) complexes of the 2,6-diacetylpyridine series with high cytotoxic activity in cisplatin resistant A2780cisR tumor cells and reduced toxicity. *J. Inorg. Biochem.* **125** (2013) 26–31.
- Li, X.-J.; Mao, P.-D.; Wu, W.-N.; Kou, K.; Liu, S.-Y.; Wang, Y.: Ni(II)/Cu(II) complexes with two pyrrole thiosemicarbazone ligands: Crystal structures and DNA interaction. *Chin. J. Inorg. Chem.* **33** (2017) 1257–1265.
- Zhu, T.-F.; Shen, S.-S.; Lu, Q.; Ye, X.-P.; Ding, W.-L.; Chen, R.-H.; Xie, J.; Zhu, W.-J.; Xu, J.; Jia, L.; Wu, W.-N.; Ma, T.-L.: Design and synthesis of novel *N*(4)-substituted thiosemicarbazones bearing a pyrrole unit as potential anticancer agents. *Oncol. Lett.* **13** (2017) 4493–4500.
- Bermejo, E.; Castineiras, A.; Perez, T.; Carballo, R.; Hiller, W.: Synthesis and structural characterization of metal complexes of 2-formylpyrrole-4-*N*-ethylthiosemicarbazone (4EL₁) and 2-acetylpyrrole-4-*N*-ethylthiosemicarbazone (4EL₂). *Z. Anorg. Allg. Chem.* **627** (2001) 2377–2385.
- Lobana, T. S.; Kumari, P.; Zeller, M.; Butcher, R. J.: The influence of the substituents at N¹ nitrogen on geometry of nickel(II) complexes with heterocyclic thiosemicarbazones. *Inorg. Chem. Commun.* **11** (2008) 972–974.